PB-242 515

INVESTIGATION OF EXTRACTIVE SAMPLING INTERFACE PARAMETERS

K. J. McNulty, et al

Abcor, Incorporated

Prepared for:

Environmental Protection Agency

October 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

174028

EPA-650/2-74-089

OCTOBER 1974

PB242515

Environmental Protection Technology Series

INVESTIGATION OF EXTRACTIVE SAMPLING INTERFACE PARAMETERS

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US Department of Commerce
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Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-650/2-74-089

2.

3.
PB 242 515

4. TITLE AND SUBTITLE
Investigation of Extractive Sampling Interface Parameters

5. REPORT DATE
October 1974

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
K. J. McNulty, J. F. McCoy, J. H. Becker, J. R. Ehrenfeld and R. L. Goldsmith

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Walden Research Division of Abcor, Inc.
201 Vassar Street
Cambridge, Massachusetts 02139

10. PROGRAM ELEMENT NO.
1AA010

11. CONTRACT/GRANT NO.
68-02-0742

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency
Office of Research and Development
Washington, D. C. 20460

13. TYPE OF REPORT AND PERIOD COVERED
Final 12 month

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document is the result of a twelve month, three-phase investigative program with the intent of providing EPA with sufficient information to permit the establishment of minimum specifications for the design of continuous extractive sample interface systems. An extractive sampling interface system is the equipment associated with an instrumental soure measurement system which extracts, transports, and conditions a sample of the source effluent. The work in this program was directed toward an investigation of interface systems for use on Category I sources for the following instrumental techniques: 1) non-dispersive infrared analyzers, 2) ultra-violet analyzers, 3) electrochemical sensors, and 4) chemiluminescent analyzers. Both laboratory and field results are reported.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Monitoring, Stack gas	interface systems	
SO_2 - emission measurement	sampling systems	
NO_x - emission measurement	stack sampling	

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT
Release Unlimited

19. SECURITY CLASS *(This Report)*

20. SECURITY CLASS *(This page)*

21. NO. OF PAGES
191

22. PRICE
7.00/2.25

EPA Form 2220-1 (9-73)

EPA-650/2-74-089

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Contract No. 68-02-0742
ROAP No. 26AAP
Task 27
Program Element No. 1AA010

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Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

October 1974

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FORWARD

This document is the result of a twelve month, three-phase investigative program with the intent of providing EPA with sufficient information to permit the establishment of minimum specifications for the design of continuous extractive sampling interface systems. An extractive sampling interface system is the equipment associated with an instrumental source measurement system which extracts, transports and conditions a sample of the source effluent. The work in this program was directed toward an investigation of interface systems for use on Category 1 sources for the following instrumental techniques:

a. non-dispersive infrared analyzers (NDIR)
b. ultra-violet analyzers (NDUV)
c. electrochemical cell analyzers
d. chemiluminescent analyzers

Specifically, this program was charged with performing a survey of source monitor manufacturers to obtain information on their respective analyzers and the commercial products required in their sampling systems. This information would then be used to provide a basis for the specification of all the sampling system requirements for each analytical technique. This activity was Phase I of the program. Phase II involved a laboratory study of gas sample losses in various components of the sample interface system, particularly:

a. possible gas-solid reactions that could occur on particulates collected on the probe tip filter
b. sample losses or gas-phase reactions within the sample lines
c. gas interactions within various moisture removal systems

Additionally, the feasibility for calibrating the total source measurement system through injection of calibration gases at the probe inlet was investigated. On completion of Phase II, an Interim Report was submitted which included the results of laboratory studies and contained sampling system design information to be used by EPA personnel.

Phase III of the program was charged with demonstrating by field measurement an adequate sampling system for each analytical technique. The objective of these field tests was to locate potential operational problems, correct these problems and demonstrate one month of continuous operation. During continuous operation only normal maintenance was to be permitted, and calibration checks were to be performed automatically and through the filter probe, if feasible.

This final report is presented in two parts. This structure best reflects the dual (design criteria and field demonstration) aspects of the program.

Part One contains the information presented in the above-mentioned Interim Report, modified to include results of the Phase III field program. It is intended to stand alone as a source of design information for interface systems. Presently there is no other single reference source available on the design of the sampling system with this amount of quantitative engineering data.

In order to conform with present EPA report requirements for the use of SI units (Systemé International d'Unité), the data presented in the Interim Report in the usual engineering units have been converted to SI units for presentation in Part One. These units will undoubtedly be inconvenient to the reader; since units such as kilo-Newtons per square meter (kN/m^{-2}) will not impart the same physical sense as the equilivent inches (or even centimeters) of water. However with experience (and conversion tables) the SI units should not be any serious impediment to the designer of interface systems.

Part Two of this report relates the experience of demonstrating "minimum" type sampling systems in the field. This part is not independent of Part One since the demonstration systems implemented were designed based on the information presented in the Interim Report, (See Part One).

In assessing the contribution of this program to the state-of-the-art, it is felt that several contributions have been made, particularly in the use of low-cost sampling lines, a lower-cost probe-tip filter approach, less severe moisture removal requirements and calibration of the measurement system through the probe tip filter. It is somewhat disappointing that all elements of a "minimum" type sampling system have not been successfully demonstrated. Further work is required to specify "minimum", yet reliable techniques for moisture removal and for sample pumping. In this context the wouldbe designer of a new sampling interface system has through this report a considerable data base for sampling system design. However, any new system which does not reproduce an existing successful system will contain experimental elements. There remains no "algorithum" for designing "minimum" sampling systems.

ACKNOWLEDGEMENTS

In performing a program of this type one is grateful for the assistance and wisdom of others. Principal acknowledgement in this regard is to Mr. James B. Homolya of EPA who was the prime mover for initiating this investigation and served as the Technical Project Officer for the program. In the collection of information on existing practice we gratefully acknowledge the helpful discussions with the representatives of many manufacturers of sampling instruments and industrial users of source monitoring equipment. We are particularly grateful to Mr. Robert Saltzman of DuPont who was responsible for loaning to the program a DuPont Model 400 NDUV analyzer plus freely contributing his knowledge of sample interface systems in response to our many questions. The field program was helped by the cooperation of the Boston Edison Company and The Public Service Company of New Hampshire who provided test sites. We express our gratitude to these companies and their employees for their assistance to this program. At Walden we would like to acknowledge the efforts of Mr. Roger Lisk who in the course of his technican duties was exposed to the hardships and discomforts of the worst kind of New England Winter weather.

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INVESTIGATION
OF
EXTRACTIVE SAMPLING INTERFACE PARAMETERS

PART I

DESIGN DATA AND INFORMATION

SUMMARY

Design of an adequate extractive interface for the continuous monitoring of NO_x and SO_2 from Category I sources involves a number of engineering choices and trade-offs. The objective of this program is to examine the choices available and to provide information pertinent to the design of an adequate sampling interface. An "adequate" or a "minimum" sampling interface is the simplest and least expensive system that will permit continuous monitoring within certain specified tolerance limits.

The design of a sampling interface must be predicated on the specific source/analyzer combination for which it is intended. Typical source characteristics are given for power plants, nitric acid plants, and sulfuric acid plants. The sample conditioning requirements are given for eight commercially available analyzers including NDIR, UV, electrochemical, and chemiluminescent instruments.

Although it is difficult, in the absence of field test data, to recommend a specific system which will achieve an overall cost minimum, a number of design options are presented and discussed in relation to the "minimum" design criteria.

Most analyzers are sensitive to pressure changes, and some means must be provided for controlling the pressure at a fixed value. The simplest method of controlling pressure is to vent the analyzer to atmosphere. Barometric pressure variations are well within the tolerance limits for accuracy.

Sample flow rate is not a critical parameter and the need for flow control devices or back-pressure regulators is not anticipated. A flow rate on the order of 1 slpm is typical of the analyzers surveyed.

Sample temperature is not a critical parameter as long as it remains within fairly wide limits. All analyzers which are sensitive to sample temperature provide internal control.

In order to control pressure by venting to atmosphere, the sample pump must be positioned upstream of the analyzer. However, several alternatives are still available for the positioning of the pump in relation to other interface components. Advantages and disadvantages for these alternatives are discussed.

The proper choice of materials of construction is an important part of the interface design. Information is presented on the chemical resistance, heat resistance, and cost of various materials. Of the less expensive materials, polypropylene appears to be quite suitable for extensive use, except where concentrated sulfuric or nitric acid is encountered.

For combustion sources, coarse filtration is required before the sample is withdrawn from the stack. Two types of filters can be used: 1) the "external" or exposed filter in which the filter element is supported within the stack and sample passes through the filter to the sample line, and 2) the "internal" or in-line filter which is also supported within the stack but is exposed only to the withdrawn sample. (These are illustrated in Figure I-5, p. 42). The internal arrangement is recommended when calibration gases are to be injected at the probe-tip. Internal filters are available in sizes sufficient to collect particulates over a period of several months. Therefore, automatic or semi-automatic back-flushing of the filter is unnecessary. The pressure drop across a loaded alundum thimble was found to be quite acceptable.

Calibration of the analyzer by injection of zero and span gases at the probe tip was successfully demonstrated in pitot plant tests. The requirement of once-daily automatic calibration is met by using a simple timing device to actuate solenoid valves.

Information is provided for proper sizing of sample lines. For a typical analyzer flow rate on the order of 1 SLPM, 6.35 mm OD tubing is recommended. The sample line response lag is on the order of half a minute.

The rate of heat transfer from sample lines is determined and is shown to be fairly rapid. Less heat resistant plastic materials can be used for sample lines, except for the first few meters in the vicinity of the stack when sampling hot combustion gases. Unheated, self-draining sample lines are recommended where condensate freeze-up is not a potential problem. Heated, self-draining lines are recommended for sub-freezing ambients, with heating sufficient to hold the sample line temperature above 0°C. It is impractical to use high sample flow rates in unheated or uninsulated lines to prevent condensate freeze-up.

The tolerance limit on system response can be easily met without extracting excess sample and by-passing the excess to vent. Equations and procedures are given for calculating the system response time. It is shown that under practical conditions, dead-end volumes have little effect on response time. Large mixing volumes, however, can have a significant effect.

When pressure is controlled by venting to atmosphere, the two most suitable types of sampling pumps are the bellows pump and the diaphragm pump. Both are available in sizes which meet specifications for sampling system use.

Moisture removal is an important part of the interface design. Only NDIR instruments require the maintenance of a constant moisture level. A refrigerated condenser is recommended for most applications. Where absorption of NO_2 by the condensate is a potential problem, a permeation dryer can be used or, in some cases, the sample can be maintained above its dew point. The use of dessicants is not recommended. Various condensate traps and removal schemes are discussed. The simplest appears to be a ball-float trap when operated under positive pressure and a barometric trap when operated under negative pressure. Information is given on the temperature-pressure requirements to prevent condensation in the analyzer.

The considerations involved in fine filtration are discussed. A number of filter media will give good particulate removal, including a tube packed with glass wool.

Sophisticated instrumentation is not required. Useful measurements include the sample flow rate, the pump suction and discharge pressures, and the condenser temperature. If heated sample lines are used, sample line temperatures are also useful.

Some modifications of the above general design considerations are required for different source and analyzer combinations. These modifications are discussed. Methods of demisting sulfuric acid stack gases are also considered.

Information is provided on commercial sources of various components suitable for use in sampling systems, and the specifications are given for the interface to be demonstrated in field tests.

An important requirement of any sampling interface is that interactions between the interface and sample must not exceed certain tolerance limits. Three types of interaction, viz., reaction, absorption, and adsorption, are considered in detail.

Loss of SO_2 by catalytic oxidation to SO_3 on particulates collected in the probe-tip filter has been shown to be negligible both by calculation and by experiment. Loss of NO by gas phase oxidation to NO_2 can be appreciable if the residence time within the sampling system is very long. However, under normal sampling conditions, the loss of NO will be within the tolerance limits on accuracy. Catalytic oxidation of NO on probe-tip particulates was shown, by experiment, to be negligible. Loss of NO_2 by reduction is not anticipated.

Loss of SO_2 by absorption (dissolution) in condensate is shown to be negligible both by calculation and experiment. The solubility of NO is much less than SO_2 and losses are again negligible. On the other hand, NO_2 is very soluble and, if equilibrium is reached, complete NO_2 loss can occur. However, this is of little concern in most monitoring applications. Combustion stack gases typically contain only a few percent of the total NO_x in the NO_2 form, and complete loss will not exceed the tolerance limit which is set on NO_x. In the few applications where significant NO_2 concentrations are expected, means are recommended for eliminating absorptive losses.

Adsorption on interface components can effect the system response time. Experimental tests on various sample lines indicated negligible adsorption effects for Teflon, 316 SS, and polypropylene; small effects for nylon; and large effects for polyethylene and Tygon. The latter two are not recommended for extensive use in sampling systems.

INTRODUCTION

Under authority of the Clean Air Act, the U.S. Environmental Protection Agency has set forth standards of performance for new and modified stationary sources (1). Table I-1 lists the sources covered, the limitations placed on various pollutants, and the requirements for monitoring. Continuous monitoring of NO_x and/or SO_2 is required for power plants, nitric acid plants, and sulfuric acid plants.

TABLE I-1

FEDERAL REGULATIONS FOR STATIONARY SOURCE EMISSIONS

Source	Pollutant	Limit	Continuous Monitoring Required?
Steam Generators			
Gas Fired	Particulates	0.043 kg/G joule	Yes[b]
	NO_x	0.086 kg/G joule[a]	Yes
Oil Fired	Particulates	0.043 kg/G joule	Yes[b]
	SO_2	0.344 kg/G joule	Yes[c]
	NO_x	0.129 kg/G joule	Yes
Coal Fired	Particulates	0.043 kg/G joule	Yes[b]
	SO_2	0.516 kg/G joule	Yes
	NO_x	0.301 kg/G joule	Yes
Nitric Acid Plant	NO_x	1.5 gm/kg acid[a]	Yes
Sulfuric Acid Plant	SO_2	2.0 gm/kg acid	Yes
	H_2SO_4 mist	75 mg/kg acid	No
Incinerators	Particulates	.1668 mg/sl	No
Portland Cement Plant	Particulates	150 mg/kg kiln feed[d]	No
		50 mg/kg kiln feed[e]	

(a) Expressed as NO_2

(b) Continuous monitoring by smoke detector

(c) Except where low sulfur fuels are burned and representative daily sulfur analyses are performed

(d) Emission limit on kiln

(e) Emission limit on clinker cooler

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In order to continuously monitor stack gases, an analyzer must be used which is capable of providing an electronic output that is proportional to the concentration of pollutant in the sample stream. However, even the best of analyzers cannot provide reliable monitoring without a properly designed sampling interface. The sampling interface must be capable of performing the following functions:

- Removing a representative sample from the stack;
- Maintaining sample integrity (within specified limits) during transport to the analyzer;
- Conditioning of the sample for compatibility with the analyzer;
- Providing gas switching to calibrate the analyzer.

Although there are a number of commercially available extractive sampling interfaces, the rationale behind the particular designs used has not been thoroughly reported or examined. The objective of this program and of this report is to provide information pertinent to the design of SO_2 and NO_x extractive sampling interfaces with particular emphasis on design criteria for a "minimum" system. In this respect, a minimum sampling system may be defined as the simplest and least expensive system that will permit analysis within certain specified tolerance limits over an "acceptable" period of time.

There are several tolerance limits which are particularly applicable to the design of stack sampling interfaces:

- Accuracy must be within ± 10% based on the mean output and ± 20% at the 95% confidence interval. Accuracy may be determined by injection (preferably at the probe tip) of zero and span gases or by verification with wet chemical analysis.
- System response must be 95% complete within eight minutes. System response may be determined by injection at the probe of a step change in concentration and measuring the time required for 95% of full response.
- The operational period must be at least seven days during which no replacement, repairs, or corrective maintenance may be performed other than routine analyzer adjustments.
- The analyzer must be automatically recalibrated once every 24 hours by injection of zero and span gases at the probe tip, if feasible.

Other limits such as zero drift, calibration draft, and repeatability are more directly applicable to the analyzer operation and will not be considered as limitations on the design of the sampling interface.

In addition to the above limitations, the design of the sampling interface will be strongly influenced by the source/analyzer combination. The obvious design procedure is:

1. determination of source characteristics at the most feasible sampling sites,
2. select the best sampling site,
3. determine the requirements of the analyzer, and,
4. design an appropriate sampling interface that will provide the analyzer with a compatible sample.

SOURCE CHARACTERISTICS

The three sources of particular interest in relation to federal rerequirements for continuous monitoring are power plants, nitric acid plants, and sulfuric acid plants. It is, of course, impossible to provide precise information on the temperature and composition of stack gases from each of these sources. The stack gas characteristics depend on a wide range of operating variables and are strongly influenced by emission control processes. The design of a sampling interface should be predicated on information from the specific source for which it is intended. Nevertheless some "typical" values can be presented and some general comments made.

POWER PLANTS

The major stack gas constituents resulting from combustion of fossil fuels can be easily approximated from an assumed fuel composition and an assumed excess of air. The assumptions and calculations are given in Appendix A. The results for gaseous, liquid, and solid fossil fuels are given in Table I-2. The typical maximum emissions are based on the Federal standards given in Table I-1

More detailed information is available on emissions from coal fired (2) and oil fired (3) power plants. This data gives actual emissions for various facilities, fuels, and operating procedures.

NITRIC ACID PLANTS

Most nitric acid is produced by the "pressure" process in which an ammonia-air mixture under pressure is catalytically oxidized to NO and NO_2. The NO_2 is subsequently absorbed in water to form nitric acid. The tail gas containing NO and unabsorbed NO_2 from the absorber is the primary source of NO_x emissions from nitric acid plants. Table I-3 gives typical stack gas characteristics from two plants: one with no further treatment of absorber tail gases and one using catalytic reduction to convert NO and NO_2 to nitrogen. Catalytic treatment involves mixing the tail gases with a fuel such as hydrogen or natural gas and passing the mixture through a reactor. The nitrogen oxides are reduced to nitrogen and the fuel is oxidized to combustion products (CO_2 and H_2O).

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Catalytic treatment of waste gases is by far the most commonly used method of reducing NO_x emissions. However, it is also possible to remove NO and NO_x by caustic absorption to form nitrite and nitrate salts. In this case, the stack gases will have approximately the same composition as the gases from a plant with no waste gas treatment except that the concentration of NO_x will be reduced by about an order of magnitude.

SULFURIC ACID PLANTS

Most sulfuric acid is produced by the contact process in which any one of several sulfur containing feeds (elemental sulfur, hydrogen sulfide, sulfide ore, spent sulfuric acid, etc.) is oxidized to SO_2 in a sulfur-burning furnace. The SO_2 is mixed with air and catalytically oxidized to SO_3. The SO_3 is then absorbed in 98 to 99 percent sulfuric acid. The tail gas from the absorber is the primary source of emissions from sulfuric acid plants. Typical stack gas compositions are shown in Table I-4. Note that there is essentially no free water in the stack gases leaving the absorber. The typical emission limits are again based on the federal standards. It is obvious that some means of emission control must be used to reduce SO_2 and H_2SO_4 mist.

Many types of SO_2 recovery systems have been proposed but until recently only a few such systems have been installed. Alkaline scrubbing has been used to reduce SO_2 to about 300 ppm in two stages. The use of any type of wet scrubbing process will saturate the stack gases with water at the prevailing conditions within the scrubber.

TABLE I-2

STACK GAS CHARACTERISTICS FOR FOSSIL-FUEL FIRED POWER PLANTS

	Gaseous Fuel	Fuel Oil	Coal
Stack Temp (^{o}C)[(a)]	135-205	150-205	150-205
Typical Stack Gas Composition[(b)]			
CO_2	8%	12%	14%
H_2O	16%	9%	6%
N_2	73%	76%	77%
O_2	3%	3%	3%
Typical Maximum Emissions[(c)]			
Particulates	0.119 mg/sl	0.127 mg/sl	0.125 mg/sl
SO_2	-	394 ppm	572 ppm
NO_x	127 ppm	205 ppm	464 ppm

(a) Ref. 15

(b) Calculated on the basis of 20% excess air. Assumptions and calculations given in Appendix A.

(c) Calculated from Federal emission standards (1). See Appendix A.

TABLE I-3

STACK GAS CHARACTERISTICS FOR NITRIC ACID PLANTS

	Before Waste Gas Treatment	Catalytic Waste Gas Treatment
Gas Temperature[a]	21.1-37.8 °C	204.4-260 °C
Typical Stack Gas Composition[a]		
NO_x	0.3%	0.01%[c]
H_2O	0.7%	3.8%
N_2	96.0%	94.2%
O_2	3.0%	--
CO_2	--	2.0%
Typical Maximum Emissions[b]		
NO_x		202 ppm

(a) From Ref. 16, p. 10.

(b) Calculated from Federal emission standards (1) assuming an average stack gas rate of 3621 sl/kg acid produced (Ref. 16, p. 22).

(c) For specific installations, NO_x content may vary considerably: from .21% to <.0002% (Ref. 16, p. 22).

TABLE I-4

STACK GAS CHARACTERISTICS FOR SULFURIC ACID PLANTS

	Contact Plant with Mist Eliminator
Stack Gas Temperatures(a)	23.9 - 100 °C
Typical Stack Gas Composition(a)	
SO_2	0.26%
SO_3 and/or H_2SO_4 mist	
O_2 and N_2	99.74%
Typical Emissions Limit(b)	
SO_2	255 ppm
H_2SO_4 mist	.0272 mg/sl

(a) Ref. 17

(b) Calculated from Federal standard assuming an average stack gas rate of 2747 sl/kg acid produced (ref. 17).

ANALYZER REQUIREMENTS

The requirements of the analyzer play an important part in the design of a sampling interface. Requirements that must be considered include sample temperature, pressure, and flow rate; particulate level, moisture tolerance, and interfering species. A survey of analyzer manufacturers was conducted in order to ascertain limits on various analyzer requirements. Two manufacturers were contacted for each of the following types of monitors:

- NDIR (Beckman, Intertech)
- UV (Dupont, Teledyne)
- Electrochemical (Dynasciences, Envirometrics), and
- Chemiluminescent (Aerochem, Thermo Electron)

The results are summarized in Table I-5.

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TABLE I-5

SAMPLE CONDITIONING REQUIREMENTS FOR VARIOUS ANALYZERS

Principle	NDIR		UV	
Manufacturer	Beckman	Intertech	duPont	Teledyne
Model	864, 865	Uras 2	400	611, 612
Species	SO_2, NO	SO_2, NO	SO_2, NO_x	SO_2, NO_2
Sample Flow Rate	0.5-1.0 slpm	0.5-1.0 slpm	"not critical" (0.5-10 slpm)	"not critical" (0.5-10 slpm)
Sample Temperature	-1.11-37.8°C	10-45°C	Ambient to 204.4°C (typical 104.4°C)	Ambient to 176.7°C (typical 79.4°C)
Sample Pressure	"Approx. atmospheric"	-2.02 x 103N/m^2 to 0.103 M N/m^2	"Vacuum" to 0.446 M N/m^2	"Vacuum" to 1.48 M N/m^2
Moisture Content	Dewpoint = 1.67°C Maintain same dewpt. in sample & cal. gases	Dewpoint = 1.67°C Maintain same dewpt. in sample & cal. gases	Keep sample temp. above dewpoint	Keep sample temp. above dewpoint
Particulate Level	"clean" (probably < 1 μm)	< 1 μm	< 20 μm	< 10-20 μm
Analyzer Sensitivity to Pressure	Output directly proportional to P	Output directly proportional to P	Output directly proportional to P	Output directly proportional to P
Interfering Species	Sensitivity to H_2O = 100 to 1	H_2O	None	None

TABLE I-5 (continued)

Principle	Electrochemical		Chemiluminescent	
Manufacturer	Dynasciences	Envirometrics	Aerochem	Thermoelectron
Model	NX130, NR230, SS330	NS300	AA	10A
Species	SO_2, NO_2, NO_x	SO_2, NO_x	NO, NO_x	NO, NO_x
Sample Flow Rate	0.25-1 slpm	1-2.5 slpm	0.5 slpm automatically fixed	0.5-2.0 slpm
Sample Temperature	4.44-37.8°C	4.44-48.9°C	3.89-60°C	4.44-48.9°C
Sample Pressure	-1.49 k N/m^2 to "slightly above atmospheric"	"Approx. atmospheric"	.101 x 10^6 ± 2.66 k N/m^2 Recalibrate for other pressures	-16.4 k N/m^2 to 68.94 k N/m^2 Recalibrate for other pressures
Moisture Content	40-80% rel. hum. or sample temp. > dewpoint	Sample temp. > dew point	Dewpoint < 21.1°C	Dewpoint below analyzer temperature
Particulate Level	"Free of suspended material" (< 1 μm)	Remove 98% > 0.7 μm 100% > 1.7 μm	< 1 μm	Remove 91% > 0.6 μm
Analyzer Sensitivity to Pressure	Output directly proportional to P	Sensitive to pressure	Flow rate internally regulated	Pressure internally regulated
Interfering Species	NO_2	NO_2	Minor sens. to CO_2	

DESIGN OF SAMPLING INTERFACE

DESIGN STRATEGY

The design of a "minimum" sampling interface is not a completely straightforward problem. To be acceptable, the sampling interface must deliver a continuous sample flow that is conditioned to meet the analyzer requirements. However, there are a number of different interface designs that can perform this task. The minimum-system design is that one which represents the greatest economy in terms of capital investment, operating costs (labor) and maintenance costs. This may involve a number of trade-offs. For example, the use of cheaper materials of construction may result in a higher rate of corrosion and higher maintenance costs. Or, a highly automated system will require a larger capital investment but may save on operating costs. These trade-offs are difficult to assess in the absence of actual in-field operating data. Furthermore, a number of options are available in the placement of sample conditioning components. There may be no obvious overriding advantage for one design over another. As a result, it is unrealistic to attempt to propose a rigid sampling interface design for a particular source/analyzer combination and claim that it achieves an absolute cost minimum. Nevertheless, it is worthwhile indicating the general directions in which such a minimum lies.

Figure I-1 shows a sampling interface that simultaneously measures SO_2 (NDIR) and NO_x (electrochemical) emissions from a coal-fired or oil-fired power plant. This system is the most demanding in terms of sampling conditioning requirements and will, therefore, be used to illustrate the considerations involved in designing a sampling system. Specific interface requirements for other source/analyzer combinations will be given in the subsection entitled Specific Source/Analyzer Combinations. The strategy used in arriving at the design of Figure I-1 was to keep the system as simple as possible and to use automation only where absolutely necessary, i.e., for automatic daily calibration checks. It is reasonable to presume that the simpler the system the fewer the potential failures.

Sample is withdrawn from the stack through a probe tip filter, which removes coarse particulates, and is drawn through a sample line which, for

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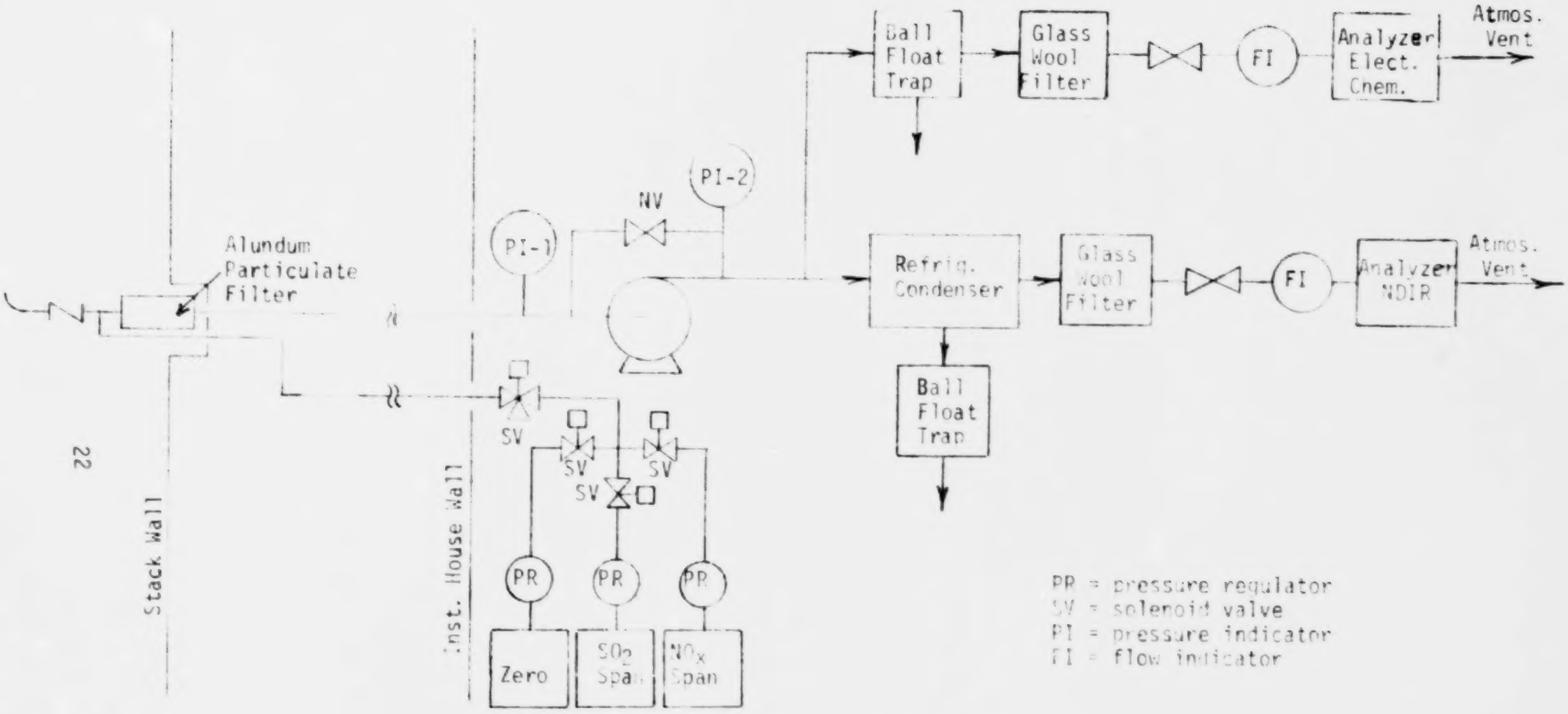
Stack Wall
Alundum Particulate Filter
Inst. House Wall
PI-1
NV
PI-2
SV
SV
SV
SV
PR
PR
PR
Zero
SO_2 Span
NO_x Span
Ball Float Trap
Glass Wool Filter
FI
Analyzer Elect. Chem.
Atmos. Vent
Refrig. Condenser
Glass Wool Filter
FI
Analyzer NDIR
Atmos. Vent
Ball Float Trap
PR = pressure regulator
SV = solenoid valve
PI = pressure indicator
FI = flow indicator

Figure I-1. Flow Schematic of Monitoring System for Combustion Sources.

outdoor service, is heated only enough to prevent freezing of condensate in the lines. The sample passes through a pump fitted with a by-pass valve to regulate the discharge pressure. For the NDIR instrument the sample then passes through a refrigerated condenser to obtain a constant low moisture level, and condensate is continuously removed by a ball-float trap. For the electrochemical instrument, only the condensate trap is necessary. A fine filter is used to remove particulates above the submicron range. The flow rate of each sample is adjusted with the needle valves, and is measured at the flow indicators before passing through the analyzers. Calibration gases are automatically injected at the probe tip once every 24 hours. The pressure at the pump suction is measured to check for excessive pressure drop across the probe tip filter and sample line; the pressure at the pump discharge is measured to check for excessive pressure drop across the fine filter and to set a reasonable pump discharge pressure.

The design requirements for each specific component in the interface will be considered in subsequent sections after a more detailed treatment of the design rationale for the overall system.

CONTROL OF SAMPLE FLOW RATE

Most analyzers are not particularly sensitive to minor variations in the flow rate; the analyzers shown in Table I-5 can typically tolerate a two- to four-fold variation in flow rate. It is interesting that the recommended sample flow rate for all of the analyzers surveyed is on the order of one standard liter per minute (SLPM). This flow rate will be used as "typical" in several subsequent design calculations.

Since sample flow rate is not a critical factor, the use of a flow controller is unnecessary. For the design of Figure 1, sample flow rate is determined by the pressure at the fine filter outlet and the setting of the needle valve upstream of the flow meter. With this arrangement, there should be only a minor long-term variation in flow rate. Potential sources of variation are: changes in pump discharge pressure due to loading of the probe tip filter, plugging of sample lines, plugging of the pump by-pass line, temperature variations, etc.; and changes in the fine filter discharge pressure due to particulate loading. It is anticipated that the flow rate variation will not exceed the allowable range (Table 5) over a seven day period.

Most commercially available sampling interfaces withdraw more sample from the stack than is actually needed by the analyzer. The excess sample is then vented through a back pressure regulator as shown in Figure 2. The by-pass flow to vent is generally several times as great as the flow rate to the analyzer. The primary advantages that may be cited for this arrangement are: (1) the response time for the sampling interface is less since a higher flow rate is used, and (2) the regulated pressure maintains a constant flow rate to the analyzer. However, it will be shown in a later section that if the sampling lines are properly sized, the 95% response time of the sampling system will fall well within the eight minute limit. Thus, the use of high flow rates for improved response is really unnecessary. Moreover, the practice of extracting excess sample has a distinct disadvantage in that filters are loaded more rapidly, sample lines plug more rapidly, corrosion and particulate destruction of pumps and other components is increased, and, in general, the maintenance costs are greater.

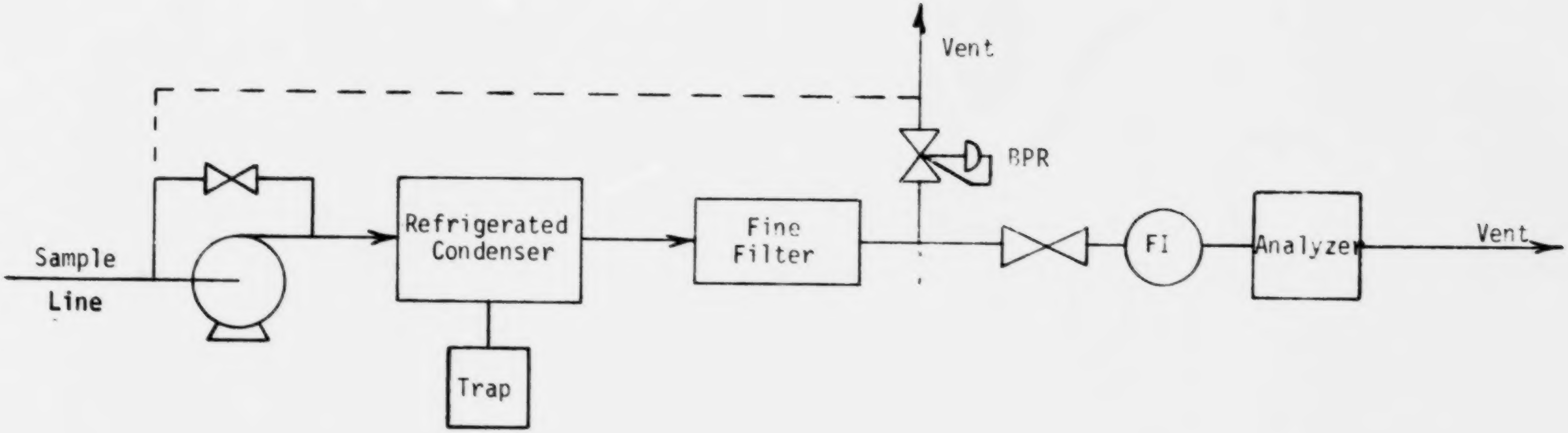
Vent
BPR
Sample
Line
Refrigerated Condenser
Trap
Fine Filter
FI
Analyzer
Vent

Figure I-2. Sampling Interface Using BRP to By-Pass Excess Flow

As pointed out previously, it is probably not necessary to use a back pressure regulator to maintain an acceptably constant flow rate to the analyzer. However, if a constant flow were required, one possible arrangement would be to use a back pressure regulator in a recirculation loop to the pump suction as shown by the dashed line in Figure II-2. In this way the pressure could be regulated without having to vent a portion of the sample. Except where maintenance of a constant flow rate is essential, the use of a needle valve is preferred to a BPR since the needle valve is simpler, cheaper, and less susceptible to malfunction.

CONTROL OF SAMPLE TEMPERATURE

Without exception, all of the analyzers surveyed had provisions for internal temperature control. Therefore, it is only necessary for the sampling interface to provide a sample within the rather wide temperature limits of Table I-5. In general, the sample temperature equilibrates quite rapidly with the surroundings (quantitative information is provided in the subsection entitled Heat Transfer from Sample Lines) so that the sample enters the analyzer at essentially room temperature. It is therefore necessary that the enclosure housing, the analyzer, and the conditioning components of the sampling interface be kept above freezing and within the temperature limits of Table I-5. There is no need to accurately control the ambient temperature at a fixed value.

CONTROL OF SAMPLE PRESSURE AND VENTING OF SAMPLE

In general, analyzers are quite sensitive to changes in sample pressure. For most analyzers output varies in direct proportion to pressure. It is therefore necessary in most cases to provide some means of pressure control at the analyzer. The simplest and most convenient means of controlling the pressure is by venting the analyzer to atmosphere. In this case, the analyzer will operate at atmospheric pressure provided the vent line is properly designed to give a negligible pressure drop.

Atmospheric pressure is, of course, subject to variation. Data on the variation of barometric pressure (4) is given in Table I-6. This data covers an 18-year period from 1946-1963 with barometric pressure readings taken once every three hours. The largest monthly variation is for the northeast region of the United States where a standard deviation of 8.75 mm of mercury was measured for the month of February. The probability that a pressure reading will fall beyond two standard deviations from the mean is less than 5% (4.55%). Therefore, at a confidence interval of 95%, the maximum pressure variation may be taken as 2330 N/m^2 or about 2.3%. This is a very small variation when compared to the allowable 20% variation at the 95% confidence interval.

The vent line will generally be fairly short (6 m or less) and even with 6.35 mm o.d. tubing, the pressure drop will be small. For example, at a flow rate of 1 SLPM, the pressure drop across 6 meters of 6.35 mm o.d. x 1.02 mm wall tubing is only 241 N/m^2. The only time this pressure drop will have any effect at all on the accuracy of the analyzer output is when different flow rates are used during calibration and sample analysis. If, for example, calibration is done at 2 SLPM and sample analysis at 1 SLPM, the pressure drop will be 482 N/m^2 during calibration giving a pressure difference of 241 N/m^2. This translates into an error of only 0.23% which is entirely negligible.

At the other end of the spectrum there may be some concern in making the vent line too large in diameter and too short. In this case, it is possible that air may diffuse back through the vent line and cause an inaccurate

TABLE I-6

BAROMETRIC PRESSURES AND STANDARD DEVIATIONS

Values in inches of mercury*, eight observations per day 1946-1963

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Alameda, Calif.	Mean	30.101	30.076	30.042	30.006	29.971	29.920	29 927	29.923	29.905	29.982	30.058	30.097	30.000
	S.D.	0.172	0.169	0.165	0.126	0.103	0.089	0.073	0.078	0.088	0.105	0.145	0.168	0.146
	Total Obs.	6184	5646	6191	6000	6200	6000	6432	6448	6239	6447	6239	6447	74473
Boston, Mass.	Mean	29.985	29.955	29.910	29.912	29.934	29.910	29.933	29.959	30.033	30.029	29.980	29.993	29.961
	S.D.	0.317	0.344	0.286	0.265	0.198	0.182	0.157	0.152	0.205	0.241	0.274	0.295	0.253
	Total Obs.	4462	4063	4460	4317	4464	4313	4464	4452	4319	4462	4317	4462	52555
Chicago, Illinois	Mean	29.366	29.339	29.275	29.247	29.269	29.250	29.296	29.313	29.341	29.345	29.299	29.343	29.307
	S.D.	0.259	0.260	0.256	0.237	0.176	0.147	0.119	0.119	0.164	0.199	0.252	0.256	0.215
	Total Obs.	4215	3834	4214	4077	4211	4053	4074	4010	3942	4395	4315	4462	49802
Miami, Florida	Mean	30.105	30.070	30.041	30.026	29.992	29.989	30.040	29.991	29.937	29.943	30.028	30.085	30.021
	S.D.	0.123	0.124	0.111	0.107	0.086	0.078	0.059	0.071	0.086	0.099	0.101	0.102	0.110
	Total Obs.	5698	5196	5701	5517	5704	5515	5702	5454	5279	5455	5279	5455	65955

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[*] To convert inches of mercury to Newtons/square meter, multiply values by 33874.

analyzer reading. However, calculation of the rate of back-diffusion against flow indicates that this is an extremely unlikely possibility. It is fair to assume that at the point where the vent line attaches to the analyzer sufficient restriction has been provided to prevent atmospheric back-diffusion.

It is important in installing the vent line to consider the possibility of moisture condensation. If the sample is vented outdoors where the temperature is below the dewpoint of the sample, i.e., the temperature of the condensate removal trap, condensation will occur. Condensate may run back through the vent line into the analyzer causing severe problems or, if outside temperatures are low enough, the condensate may freeze and plug the vent line. Outdoor vents should be as short as possible and pitched so that condensate runs away from the analyzer rather than toward it, as shown in Figure I-3. Alternatively, liquid condensate can be handled by a barometric trap as shown in Figure I-3. The trap should be filled with water before startup so that samples are not vented within the instrument enclosure. A third alternative, shown in Figure I-3, is to heat trace the portion of the vent line which extends beyond the instrument housing. The short pitched vent is the simplest of the three alternatives.

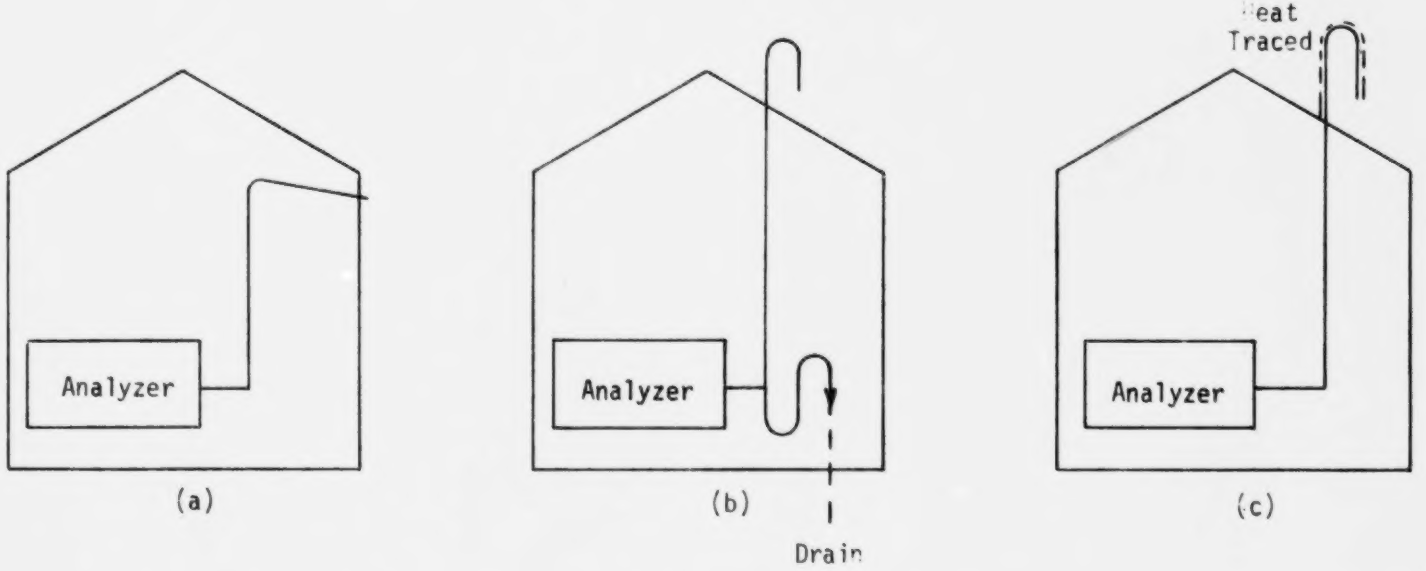

Analyzer
(a)
Analyzer
(b)
Drain
Heat
Traced
Analyzer
(c)

Figure I-3. Alternatives for Sample Venting to Atmosphere;
(a) Pitched line; (b) Barometric trap;
(c) Heat traced vent.

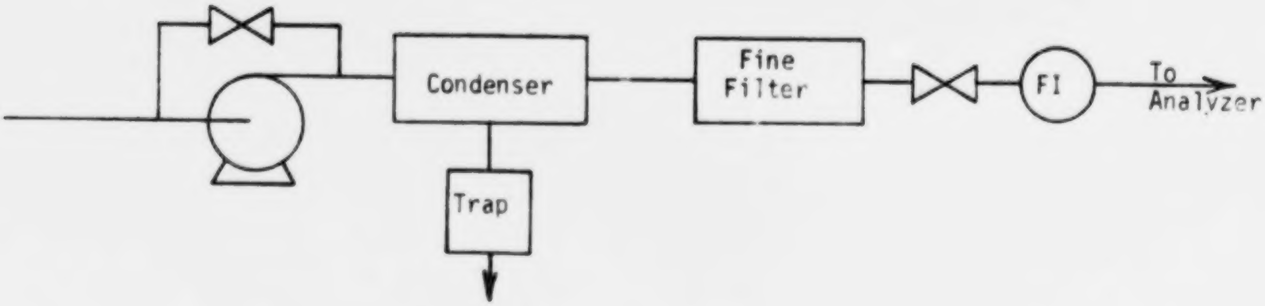
POSITIONING OF SAMPLE PUMP

There are a number of options available in the placement of sample conditioning components for a given source/analyzer combination. The arrangement shown in Figure I-1 is only one of several possibilities. It is difficult,in the absence of in-field operating experience to properly weight the advantages and disadvantages of each arrangement. Nevertheless, it is worthwhile pointing out these advantages and disadvantages and making some qualitative comments.

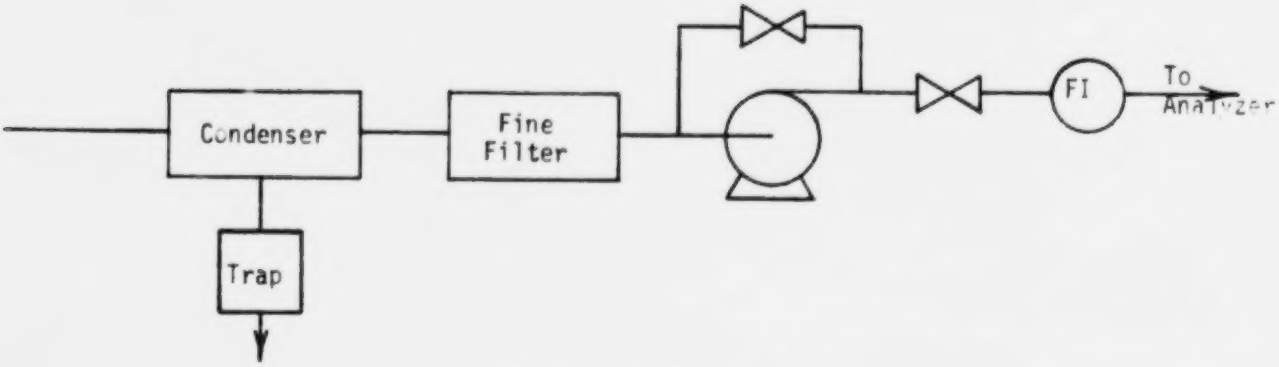
One major alternative lies in the placement of the sampling pump. Two different arrangements are shown in Figure I-4. Other pump positions are also possible. For example, the pump may be placed downstream of the analyzer in which case the sample would be "pulled" through the entire system rather than "pushed". This alternative would require a more elaborate means of pressure regulation at the analyzer and also maximizes any air in-leakage that may occur. However, for the chemiluminescent analyzers, which have built-in flow control provisions, this is the preferred arrangement (see the subsection entitled Specific Source/Analyzer Combinations).

For the two alternatives shown in Figure I-4, the following advantages may be listed for alternative A (pump upstream of condenser and fine filter).

(1) Condensate removal occurs at the point of highest pressure in the monitoring system and is therefore more complete than in alternative B. The mole fraction of water vapor in the sample is equal to the vapor pressure of water at the condenser temperature (or trap temperature if no condenser is required) divided by the total pressure. Thus, the amount of water vapor in the sample is inversely proportional to total pressure. If, for example, the pressure at the condenser is 13790 N/m^2 for alternative A and -6895 N/m^2 for alternative B there will be 18% less moisture in the A sample. This difference in moisture levels will probably be of little consequence even for analyzers which are sensitive to water vapor. However,


Condenser
Trap
Fine Filter
FI
To Analyzer

Alternative A


Condenser
Trap
Fine Filter
FI
To Analyzer

Alternative B

Figure I-4. Alternatives for Positioning of Sample Pumps

for alternative B the analyzer operates at a higher pressure than the condenser (or trap) and care must be taken to operate the analyzer at a higher temperature also in order to prevent condensation (see the subsection entitled Moisture Removal).

(2) The possibility of air in-leakage is minimized since the condenser, trap, and fine filter are under pressure rather than vacuum as in alternative B.

(3) Since in alternative A the condensate removal trap is under positive pressure a simple ball float trap can be used to continually remove condensate. For alternative B, a barometric leg must be used, or the trap must be intermittently pressurized to remove condensate (see the subsection entitled Moisture Removal).

The advantage of alternative B is that the pump is protected from both liquid condensate and particulate matter. It may turn out that this is an over-riding advantage. Field experience gained by the Thermoelectron Corporation (5) indicates that the pump is the one component most prone to failure. For this reason they strongly prefer alternative B. On the other hand, Beckman Instruments (6), Leeds and Northrup (7), and others use alternative A for sampling combustion sources. In the field tests to be conducted in Phase III of this project alternative A in Figure I-4 will be used initially. If rapid pump failure occurs, alternative B will then be implemented.*

*The results of the work in Phase III (see Part Two) favor Alternative B over A. With experience it seems that the pump needs more protection (at least from coal-fired sample gas) than provided by alternative A.

MATERIALS OF CONSTRUCTION

The choice of proper materials of construction is a very important part of designing a sampling interface. Acceptable materials of construction must meet three criteria: (1) the materials must have sufficient chemical resistance to withstand the corrosive constituents of the sample; (2) the materials must not exhibit excessive interaction (reaction, absorption, adsorption) with the sample gases; and (3) materials used in or near the stack must be heat resistant. For a sampling system of minimum design the above criteria must be weighed in the light of material costs.

Chemical Resistance

The corrosive constituents encountered in monitoring Category I sources are: nitrogen oxides, sulfur dioxide, dilute nitric acid, dilute sulfurous acid, dilute to concentrated sulfuric acid (wet SO_3 or acid mist). The chemical resistances of various materials to these constituents have been collected from a number of sources (8-12) and are summarized in Table I-7. All materials are evaluated at room temperature and may be considerably less resistant at higher temperatures.

Of the metals, Carpenter 20 stainless is the most resistant (and also the most expensive) followed by 316 SS, 304 SS, and finally aluminum. Glass and Teflon are quite resistant to all components of the sample. PVC and Tygon are somewhat less resistant but still good for all constituents except concentrated nitric acid which is not anticipated to be present in the sampling interface. Polyethylene and polypropylene have very nearly the same chemical resistance and are acceptable for use except where concentrated nitric acid is encountered (unlikely) or where concentrated sulfuric acid is encountered (acid mist from sulfuric acid plant). Nylon is a material of apparent limited usefulness in sampling systems; while sources differ on the performance of Viton during resistance tests.

TABLE I-7

CHEMICAL RESISTANCE OF VARIOUS MATERIALS

Material	Dry SO_2	Dry NO_x	Dil. HNO_3	Dil. H_2SO_3	Dil. H_2SO_4	Conc.* HNO_3	Conc. H_2SO_4
304 SS	S (some pitting observed)	S	S	Q	U	S	U
316 SS	S	S	S (<.051)**	S	S-Q (<.508)	S (<.508)	U (>1.27)
Carpenter 20 SS	S	S	S	S	S-Q	S	S
Aluminum	S	-	S (.127-.508)	S (.127-.508)	Q (.508-1.27)	U (>1.27)	U (>1.27)
Glass	S	S	S (<.127)	-	S (<.127)	S (<.127)	S (<.127)
Teflon	S	S	S	S	S	S	S
PVC	S	S	S	S	S^a - Q^b	U	S^a - Q^b
Tygon	S	S	S^e - Q^b	S	S	Q^e - U^b	S^b - Q^e
Polyethylene	S	S	S^c - Q^b	S	S	U	Q^c - U^b
Polypropylene	S	S	S	S	S	U	Q^c - U^b
Nylon		S	S	U	U	U	U
Viton	S^c - U^d	S	S	S	S	S^d - U^e	S^d - Q^c

*High concentrations of HNO_3 are not anticipated in the sampling interface.

**Quantities in parentheses indicate corrosion rates in mm per year.

(a) Ref. 8 (b) Ref. 9 (c) Ref. 10 (d) Ref. 11 (e) Ref. 12

S = Satisfactory
Q = Questionable
U = Unsatisfactory

Heat Resistance

The heat resistance of various plastic materials is given in Table I-8. Typical stack temperatures (Table I-2) are below the temperature limit for Teflon and some may be below the temperature limit for Viton. Depending on the exact temperature at the point of extraction, these two materials are suitable, in terms of heat resistance, for use at any point in the sampling interface. Less heat resistant plastics cannot be used in the vicinity of the probe when sampling combustion sources. The rate at which stack gases cool to a temperature compatible with other plastics is generally rapid and will be considered in the subsection entitled Heat Transfer from Sample Lines.

Surface Interactions

Materials of construction can interact with the sample by catalytic reaction, bulk absorption or surface adsorption. These factors are considered in detail in the section entitled Sample Interaction with the Interface System.

The results, in relation to materials of construction, can be briefly summarized as follows. No permanent losses, e.g., by reaction, are anticipated for any of the materials listed in Table I-7. Absorption and adsorption by the walls of the system must necessarily be transient phenomena since saturation will eventually be reached and, at steady state, the correct concentrations will be measured. Sorption (both absorption and adsorption) by the interface walls will be manifest in a slower system response to changes in concentration at the probe tip. Experimental measurements of system response using sample lines of various materials indicate that adsorption and absorption are negligible for 316 SS, Teflon, polypropylene, and nylon; are moderate for polyethylene; and are large for Tygon.

Costs

Costs are an important consideration in designing a minimum system. Local distributors of various materials were contacted for list prices on 6.35 mm diameter tubes. The materials surveyed are listed in Table I-9 in order of decreasing cost.

TABLE I-8

MAXIMUM CONTINUOUS OPERATING TEMPERATURES FOR PLASTICS

Material	Maximum Temp. (°C)
Teflon	250
Viton	150
Polyethylene*	80-125.6
Polypropylene	110
Nylon	121.1
CPVC	110
Tygon*	60-82.2

---

*Depends on type used.

TABLE I-9

COSTS OF VARIOUS SAMPLE LINE MATERIALS BASED ON 100 FT OF 6.35 MM OD TUBING

Material	Wall Thickness	List Price per 30.48 m
Heat Traced Teflon	.889	350.00
Heat Traced 316 SS	1.016	325.00
Carpenter 20 SS	.889 welded	196.00
316 SS	.889 seamless	184.45
	.889 welded	80.95
304 SS	.889 seamless	113.07
	.889 welded	71.66
Viton	1.575	145.00
Teflon	.787 stiff wall	107.00
	1.575	63.00
Tygon	1.575	15.60
Aluminum	.889	11.00
Glass	8mm OD x 6mm ID	7.33
Nylon	.762	4.40
Polypropylene	.787	4.31
Polyethylene	1.016	3.70

Practical Experience

A considerable amount of practical experience on materials of construction for sampling systems has been accumulated by manufacturers of stack gas monitors, although usage may not always be based on minimum design considerations. In general, Teflon sampling lines are preferred since they are more corrosion resistant and less expensive than stainless steel. Corrosion resistant plastics are preferred (5) at least through the point where liquid condensate is removed from the system. Both 304 and 316 SS have been found (13) to adequately resist corrosion when the sample is kept above its dew point, but 304 is significantly less resistant to warm acid condensate. Acceptable materials for internal pump construction include Teflon, Viton, and 316 SS (5, 6). Ball valves have been found (5) to operate more reliably than others since the ball is wiped free of condensate and particulates with each operation.

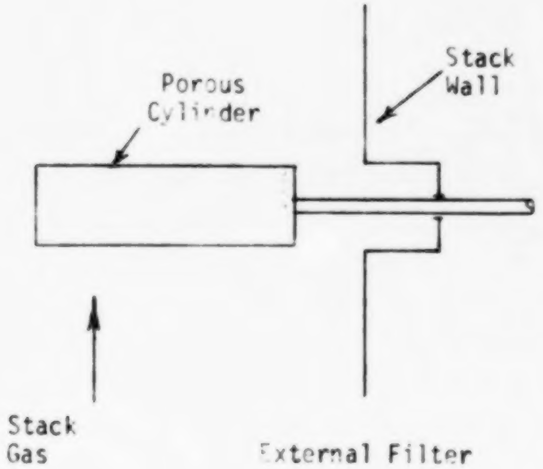
SAMPLE EXTRACTION

To obtain a representative particulate sample or acid mist sample, sampling must be done isokinetically. That is, the velocity and direction of flow into the sample-line opening must be the same as the velocity and direction of flow in the stack. However, for gas sampling it is desirable to eliminate as much particulate matter as possible at the probe inlet. This can be done by nonisokinetic sampling in which the probe opening faces downstream (toward the top of the stack). Any particulates entering the probe must then go through a directional change of 180°. This eliminates many particulates particularly in the larger size range.

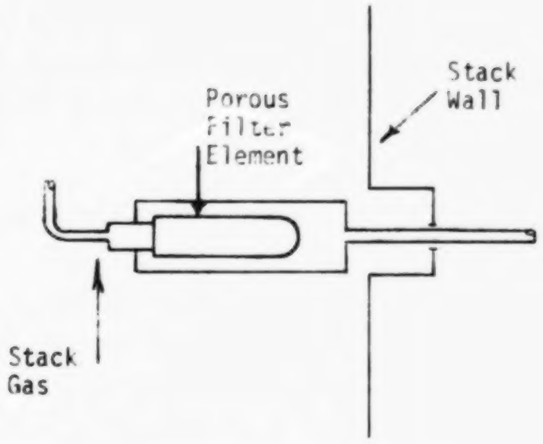
Even with the probe tip protected from direct impingement of particulates, enough fine particulate matter is carried into the sampling system to cause particulate fouling of various interface components. It is essential, for combustion source sampling, to filter the sample at the probe tip. In general there are two types of filtering arrangements that may be used: an "external" or an "internal" arrangement. These are illustrated in Figure I-5.

In the external arrangement a porous cylinder is used as the filter media. The cylinder is typically constructed of sintered 316 SS although other corrosion resistant metals may be used in addition to sintered glass, quartz, ceramic, and porous silicon carbide. It is advantageous to fabricate a semi-cylindrical baffle for the under side of the probe to protect it from direct impingement of particulates.

As an example of the availability of this type of probe tip filter, the Pall Trinity Micro Corporation manufactures three different shapes of sintered metal probe tip filters. Standard fabrication is 316 stainless steel but other materials are available including inconel, monel, nickel, 347 SS, 410 SS, other 400 SS, silver, copper, and high nickel molybdenum alloys. In the cylindrical configuration, filter areas from 0.016 to .214 sq. m. are available. Six different porosities are manufactured as listed


Stack
Wall
Porous
Cylinder
Stack
Gas

External Filter


Stack
Wall
Porous
Filter
Element
Stack
Gas

Internal Filter

Figure I-5. Probe-Tip Filter Arrangements

in Table I-10, and the pressure drop/flow characteristics for each grade are shown in Figure I-6. For a flow rate of 2 SLPM (.07 CFM) and the smallest available probe filter area (0.016 sq. m.), the flow through the filter is 118.9 l/sq m. The corresponding pressure drop for the finest available porosity is on the order of 68.95 N/m^2 for the clean filter. The filters can be regenerated to a certain extent by back flushing, and for badly clogged filters a chemical cleaning procedure is recommended. No information is available on pressure drop as a function of particulate loading in combustion stack gas monitoring. These filters are relatively inexpensive: a price of $24.45 was quoted for the cylindrical filter with 0.016 sq m. area in grade D porosity.

For the internal arrangement shown in Figure I-5, the sample passes through a probe tube before entering the filter. Any one of a number of in-line filtering devices may be used. A Western Precipation alundum thimble holder with a medium porosity thimble (pore size = 5μm) has performed very well in laboratory tests. This device has an advantage over some other filter configurations in that it permits high particulate loading with only a minimal increase in pressure drop.

The pressure drop across a clean alundum thimble is negligibly small for all normal sampling flow rates. The pressure drop for a thimble loaded to capacity with 71 grams of fly ash was measured experimentally and is shown in Figure I-7. At a flow rate of two standard liters per minute (enough to simultaneously feed two analyzers) the pressure drop is only about three inches of water.

The 71 gram capacity of the standard thimble corresponds to an operational period of 180 days assuming, as a worst case, iso-kinetic sampling at a rate of 2 SLPM of stack gas containing the typical maximum particulate concentration of .125 mg/sl (Table I-2). Thus, the alundum thimble should be able to operate for long periods without back flushing and without changing the filter element. Other filters and filter holders

TABLE I-10

FILTERING PROPERTIES OF SINTERED STAINLESS STEEL

Grade	Mean Pore Size (microns)	Removal Ratings, Microns			
		When Filtering Liquids		When Filtering Gases	
		Nominal (98%)	Absolute (100%)	Nominal (98%)	Absolute (100%)
C	165	55	160	45	110
D	65	22	55	8	20
E	35	12	35	4	11
F	20	7	25	1.3	3
G	10	3	15	0.7	1.8
H	5	2	12	0.4	1.0

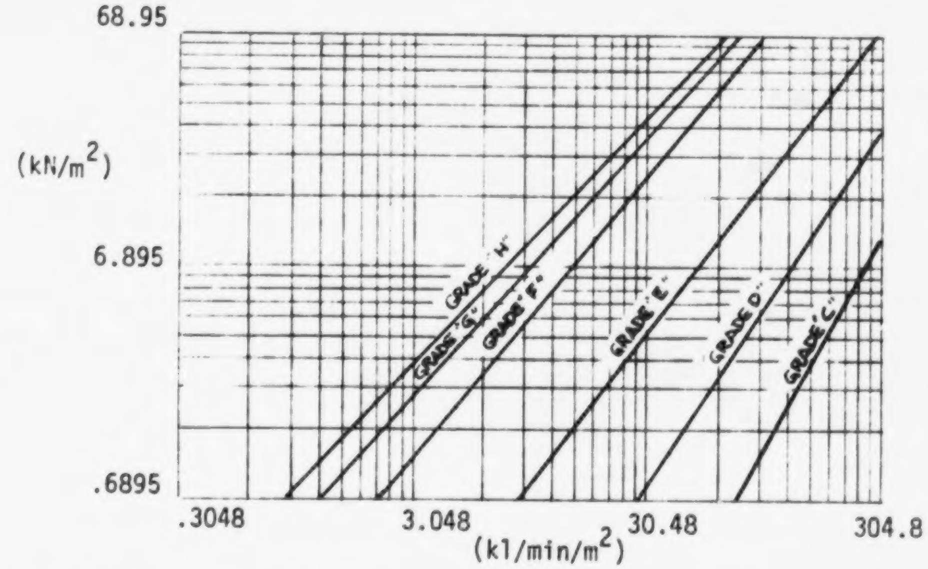


Figure I-6. Flow vs Pressure Drop for 3.18 mm Thick Sintered Stainless Steel.

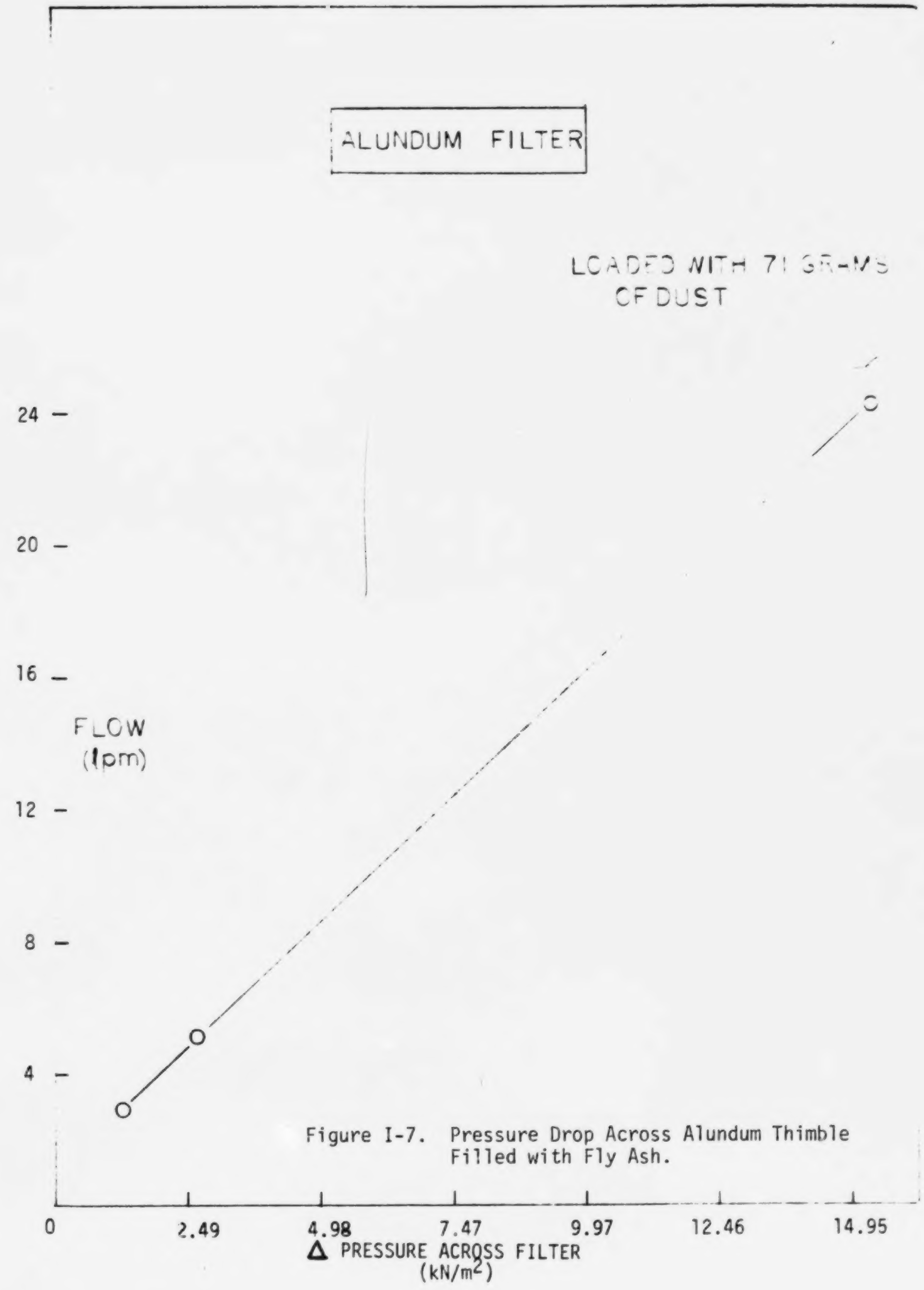


Figure I-7. Pressure Drop Across Alundum Thimble Filled with Fly Ash.

may have a somewhat lower capacity and require more frequent maintenance. However, the above results indicate that, in general, back-flushing the filter is unnecessary. Therefore, the use of automatic blow-back, as in many commercially available systems, is not recommended for a minimum design since it adds cost, complexity, and maintenance problems while providing only a minimal increase in operating convenience.*

Since combustion gases contain significant water vapor, it is very important that the filter be kept above the water dew point; otherwise, it will quickly become clogged with condensate. If the filter is placed outside the stack it may be necessary to electrically heat the filter or at least to insulate it in order to prevent condensation. This can be circumvented by placing the filter inside the stack where it is kept at the temperature of the gas sample.

An interesting alternative to the alundum thimble holder is a plug of pyrex glass wool contained in a holder made from ordinary stainless steel pipe fittings. While such a filter may be inexpensive and quite efficient in removing particulates, packing the glass wool to the correct density is a matter of trial and error. Laboratory experience has shown that a straight-through glass wool filter has a significantly higher pressure drop under loaded conditions than an alundum thimble.

Of the two arrangements shown in Figure I-5, the internal arrangement is preferred since it is much easier with this configuration to inject calibration gases upstream of the filter. For the external arrangement an elaborate injection system would have to be built in order to pass calibration gases through the filter. The internal arrangement using a alundum thimble was demonstrated in field tests.

* At the time of publishing this report, Balston Inc., Lexington, Massachusetts is bringing out a cylindrical glass fiber instack filter. This filter has about the capacity of an alundum thimble plus has a higher collection efficiency (90% at .6 μm) and reputedly a lower pressure drop. The price of the filter holder is also lower than for the alundum thimble holder.

CALIBRATION

The sampling interface requirements regarding calibration are that the system shall be automatically recalibrated once every 24 hours, and that the calibration gases (zero and span) shall be introduced upstream of the probe tip filter. The rationale behind this second requirement is that if any losses are occurring in the sampling system, e.g., catalytic oxidation of SO_2 at the probe tip filter, the same or similar losses will be experienced by the calibration gases and will be corrected for in the calibration.

Three methods were considered for calibration by injection at the probe tip:

(1) Gas flooding the filter, i.e., injecting span and zero gas ahead of the filter to a pressure greater than the stack gases.

(2) Valving off the stack gas and then injecting span and zero gas.

(3) Spiking the sample gas with a known high concentration of the test gas - known addition method.

The method suggested by (2) is the one selected for development. This approach represents some economy of span and zero gases over (1), gas flooding.

The method suggested by (3) has the advantages of calibrating the system with the minimum of span gas and using the stack gases as background. However, there are implementation problems with this method in that the concentration increase in the sample stream is given by the following:

$$\Delta C = \frac{(C'-C)q}{Q}$$

where: ΔC is the concentration increase
C' is the span concentration
C is the sample concentration
q is the span gas flow rate
Q is the gas flow through the filter

Therefore, both q and Q must be accurately known to assure calibration accuracy. This would require additional flow control equipment and instrumentation adding to the complexity and cost of the system.

Method (2) has been implemented for laboratory tests as shown in Figure I-8. A check valve is used to interrupt the sample flow when calibration gases are injected. This arrangement has worked well during the short duration of the tests. One problem that may be anticipated is the failure of the check valve to seat because of particulate buildup.* This may be circumvented by using a butterfly type check valve as shown in Figure I-9. This valve is routinely used in the pneumatic conveying of particulate solids (flour, starch, cement, etc.) and is available in PVC with a tygon seal ($22) for use below 82.2°C and in 316 SS with a viton seal for use below 204°C ($78). Teflon seals are also available for use above 121°C.

Even if the check valve fails to close completely, the calibration system of Figure I-8 can be used by operating in the gas flooding mode. It is only necessary to make sure that the calibration gases are delivered at a pressure higher than the stack pressure.

The arrangement of solenoid valves for the automatic introduction of calibration gases is shown in Figure I-1. One two-way solenoid valve is used on each calibration gas and a three-way valve is used on the line to the stack. The three-way valve is optional and may be eliminated. As will be pointed out in the subsection entitled System Response Time, it is unnecessary from the viewpoint of response time considerations to reduce the dead volume of the calibration line.

A number of options are available in the timer circuit used to actuate the solenoid valves. One simple possibility, which will be used in the field tests, is shown in Figure I-10. Two timers are used; timer #1 has a 24-hour cycle with a 15 minute on-time, timer #2 has a cycle time of 33

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* Problems with check valves sticking (closed as well as open) was found in the field tests. Experience indicates that gas flooding is more reliable and probably justifies the high consumption of calibration gases.

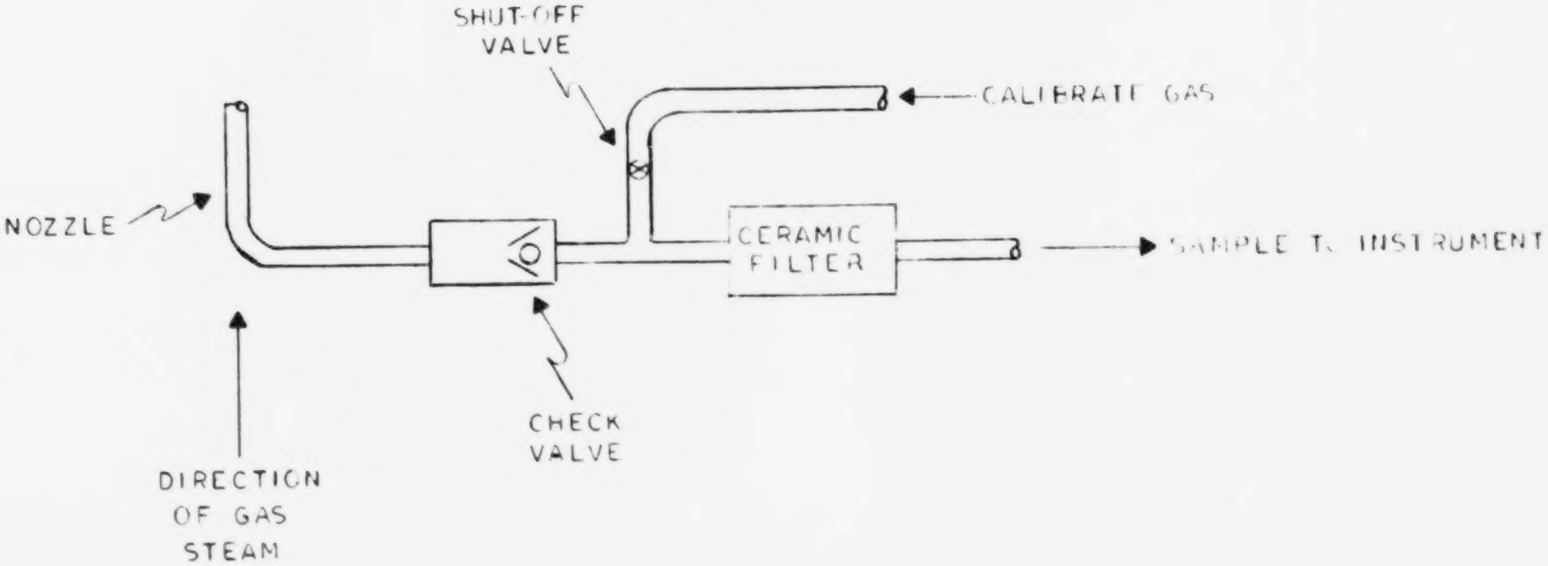

SHUT-OFF VALVE
CALIBRATE GAS
NOZZLE
CERAMIC FILTER
SAMPLE TO INSTRUMENT
CHECK VALVE
DIRECTION OF GAS STEAM

Figure I-8. Through the Probe Tip Filter Calibrate System.

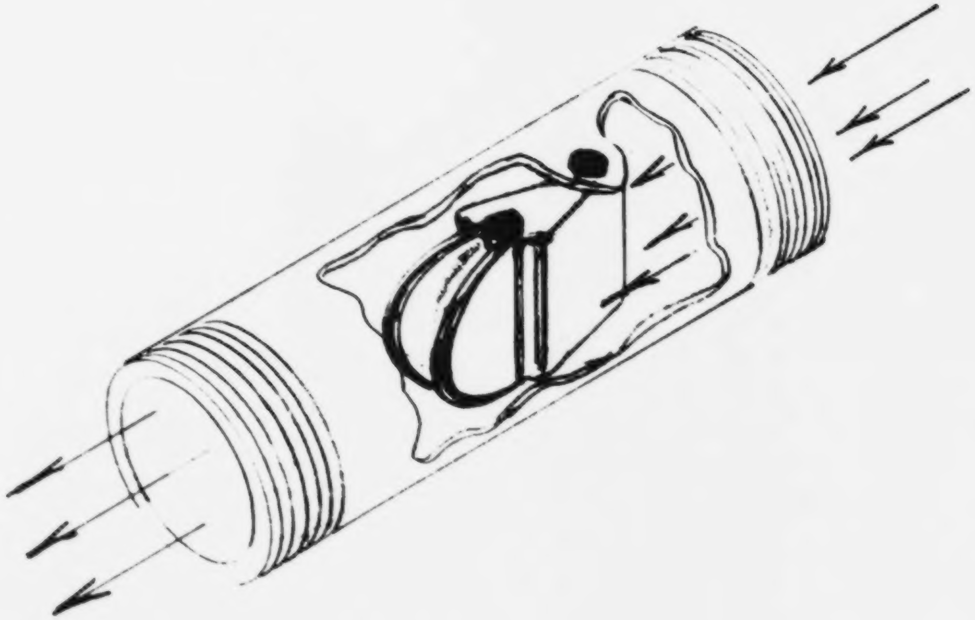


Figure I-9. Technocheck Check Valve (Techno Corporation, Erie, Pa.).

minutes and independently times four events. The operating sequence is given in Figure I-10. Calibration can also be done manually using the toggle switches shown, and pilot lights indicate when calibration gases are flowing.

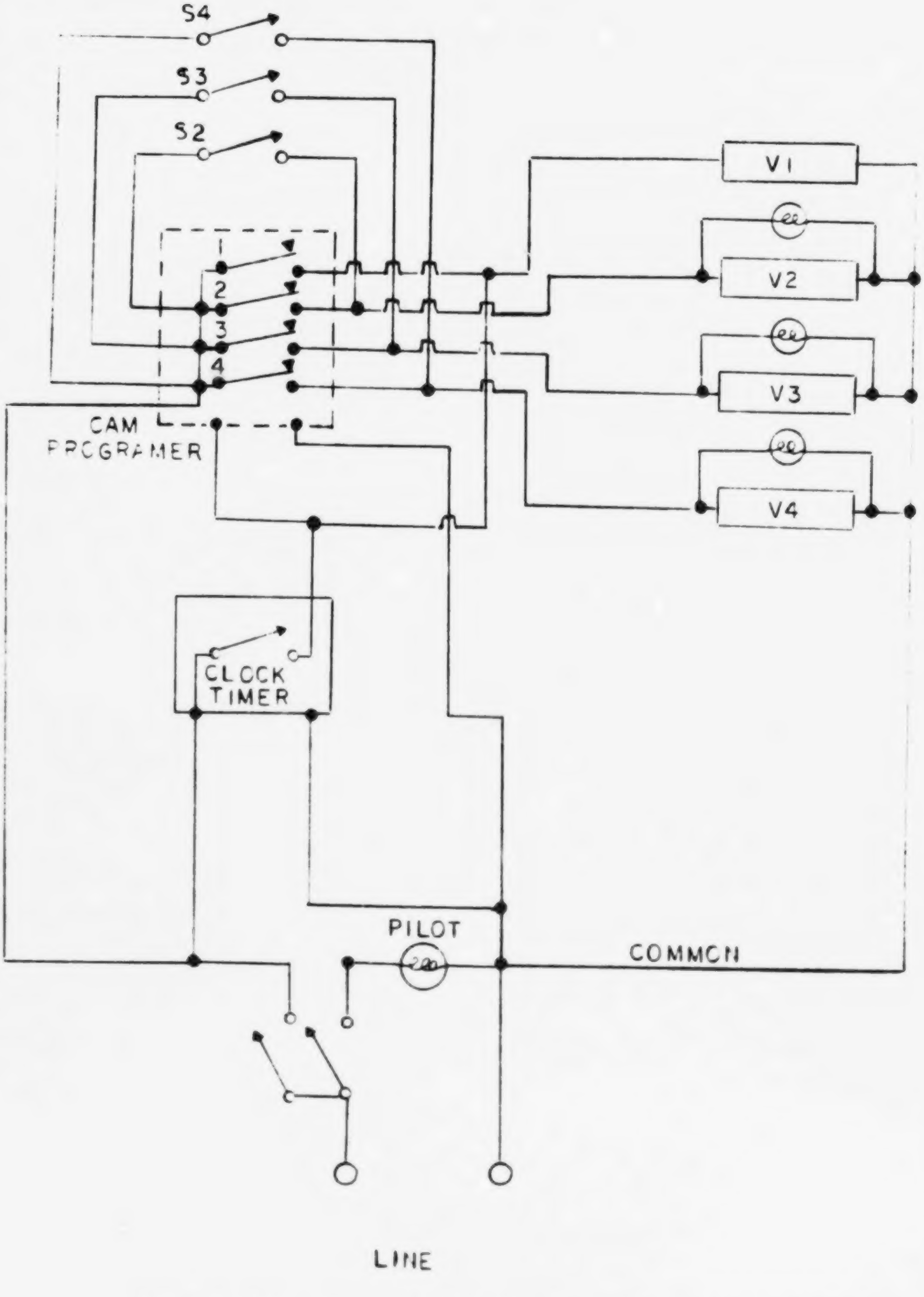

S4
S3
S2
1
2
3
4
CAM
PROGRAMER
V1
V2
V3
V4
CLOCK
TIMER
PILOT
COMMON
LINE

Figure I-10. Schematic of Timers for Automatic Calibration.

Figure I-10 (continued). Sequence of Operations.

(1) Clock timer - 24 hour cycle. On for 15 min, off for 23 hours 45 min. Actuates cam timer.

(2) Cam programmer - 33 minute cycle

Contact #1: On 30 min, off 3 min. Allows motor of cam timer to operate after clock timer opens. Actuates three-way solenoid valve (V-1).

Contact #2: On for 10 min, off for 23 minutes. Operates solenoid valve V-2.

Contact #3: Off for 10 min, on for 10 min, off for 13 min. Operates solenoid valve V-3.

Contact #4: Off for 20 min, on for 10 min, off for 3 min. Operates solenoid valve V-4.

SIZING OF SAMPLE LINES

Two considerations must be kept in mind when specifying the size of sample lines. For a given required flow through the line the diameter must be large enough so that the pump can handle the pressure drop and yet small enough so that the response time is not excessive.

Flow rate as a function of pressure drop is shown for various line sizes in Figure I-11. The assumptions and equations used in calculating these results are given in Appendix B. For a flow rate of two standard liters per minute, sufficient to simultaneously feed two analyzers, 6.35 mm o.d. tubing gives a pressure drop between 1379 and 2758 N/m^2 per 30.48 m of tubing (depending on the tube wall thickness). This pressure drop is quite acceptable for most sampling pumps. 3.175 mm tubing could conceivably be used but it is less convenient to work with and may not be readily available in some materials of construction (e.g., heat traced Teflon). It is therefore recommended that 6.35 mm o.d. sampling lines be used.

The response time of the sample line may be simply calculated assuming no wall effects and no axial dispersion. The lag time, t, for a sample line of volume V (liters) and flow rate F (liters/min) is:

$$t = \frac{V}{F} \qquad (1)$$

The flow rate, F, is related to the standard flow rate, F_S, as follows:

$$F = F_S \; \frac{1.8T + 492}{492} \; \frac{3774.3}{P + 37743} \qquad (2)$$

where T is the gas temperature in °C and P is the pressure in N/m^2 gauge. Table 11 gives lag times for 30.48 m of sampling line with various inside diameters for flow rates of 1 and 2 SLPM at 25°C and 202707 N/m^2. Lag times for other flow rates and lengths may be obtained by ratio. For the 6.35 mm o.d. tubing a lag time of about 30 seconds or less may be expected for a 1 SLPM flow. This is considerably less than the allowable eight minutes for 95% response. It would therefore appear that 6.35 mm o.d. tubing is acceptable both from the point of view of pressure drop and response time for flow rates on the order of 1-2 liters per minute.

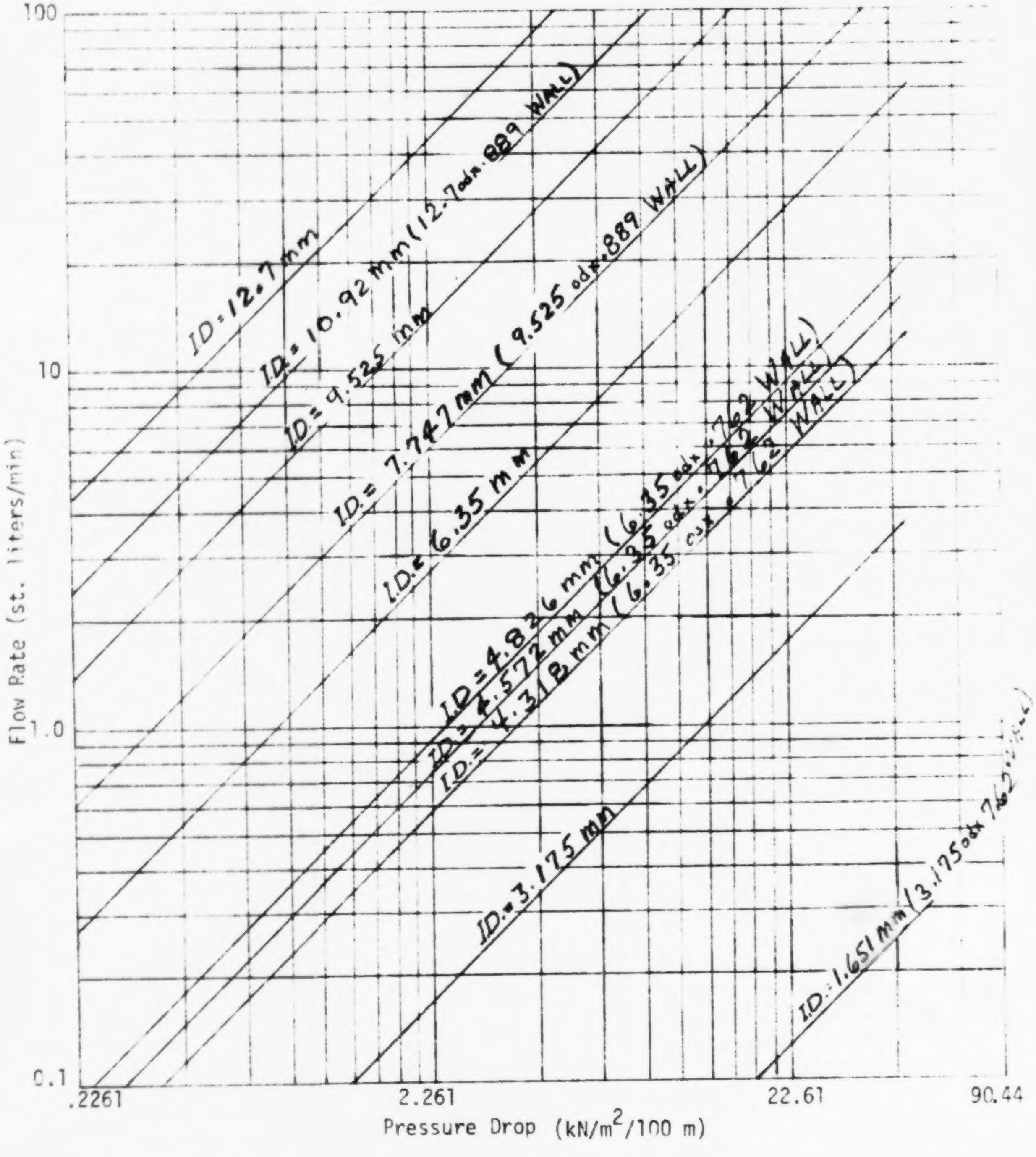


Figure I-11. Flow Rate vs Pressure Drop for Various Line Sizes.

TABLE I-11

SAMPLING LINE LAG TIME

	Lag Time per (30.48 m) Length	
Tubing Size	1 st. liter per min	2 st. liter per min
1.651 (3.175 o.d. x .762 wall)	3.58 sec	1.79 sec
3.175 (3.175 i.d.)	13.26 sec	6.63 sec
4.318 (6.35 o.d. x 1.016 wall)	24.54 sec	12.27 sec
4.572 (6.35 o.d. x 0.889 wall)	27.51 sec	13.75 sec
4.826 (6.35 o.d. x .762 wall)	30.64 sec	15.32 sec
6.35 (6.35 i.d.)	53.06 sec	26.53 sec
7.747 (9.525 o.d. x .889 wall)	1.32 min	0.658 min
9.525 (9.525 i.d.)	2.00 min	0.995 min
10.92 (12.70 o.d. x .889 wall)	2.62 min	1.31 min
12.70 (12.70 o.d.)	3.54 min	1.77 min

HEAT TRANSFER FROM SAMPLE LINES

An exact solution to the rate of heat transfer from sample lines would be quite complicated and would probably not be justified for present purposes. Reasonable approximate results can be obtained by simplified procedures. The assumptions, equations, derivations, and calculational procedures are given in Appendix C.

Three specific calculations are made in Appendix C:

(1) The rate of cooling of combustion stack gases is determined so that the feasibility of using less heat resistant materials such as polyethylene and polypropylene can be assessed.

(2) A calculation is made to assess the feasibility of using unheated sample lines in subfreezing ambient.

(3) The relative resistance to heat transfer of the tube material is determined.

Plastic materials such as polyethylene and polypropylene cannot be used in the near vicinity of the sampling probe on combustion sources because of their heat limitations (approximately 93.3°C). However, the calculations of Appendix C indicate that the sample gas cools quite rapidly. For a flow rate of 2 SLPM through 6.35 mm o.d. x 1.016 mm wall tubing with a stagnant ambient at 37.8°C, the sample cools from 260°C to 93.3°C in less than .61 meters of tubing. Therefore, the lower heat resistance of plastic materials is not a serious disadvantage and they can be used for all but the first few meters of the sample line. It should be noted that the length required for a given temperature change is proportional to the flow rate.

The use of unheated sample lines in subfreezing ambients is, in general, not feasible when the gases contain condensible moisture. The calculation of Appendix C shows that the gas sample cools from 260°C to 0°C in less than .61 meters for flow at 2 SLPM through 6.35 mm o.d. x 1.016 mm tubing in a 16.09 Km/h wind at -6.67°C. In order to prevent freeze-up and eventual plugging, the sample line must be maintained above 0°C by heating.

An interesting possibility for shortening sample lines is to locate the analyzer in a heated cabinet in the near vicinity of the sampling location and to run the output signal to the instrument house. This would be a less convenient location, however, from the standpoint of operation and maintenance. On the other hand, it would eliminate the need for long sample lines and in such cases, it may be possible to avoid the requirement of heated sample lines. Short sample lines could be insulated to a sufficient thickness, or sample flow rate could be increased to avoid freeze-up. This alternative may be useful in certain installations but is not recommended in general because of the less convenient location.

The third calculation given in Appendix C compares the resistance to heat transfer of the tube wall with the internal film resistance. For a stainless steel tube (1.016 mm wall thickness), the resistance to heat transfer is only about 0.15% of the internal film resistance. For a teflon tube of the same dimensions, the tube resistance is about 10% of the internal film resistance. Thus, the tube material has little effect on the rate of cooling of sample gases. This is particularly significant in relation to the refrigerated condenser, i.e., it is unnecessary to use a stainless steel cooling coil to obtain high heat transfer rates. Teflon or other plastics will provide nearly equal rates.

In general, it is recommended that low cost plastics such as polypropylene be used for the minimum sampling system wherever condensate freeze-up is not a potential problem, e.g., for ambient temperatures > 0°C; for dry stack gases; and for indoor lines. For locations where condensate freeze-up may occur, heat traced sampling lines are recommended. Heat traced teflon is commercially available in packaged form and probably represents an overall economy over fabrication of heat traced lines from cheaper materials.

To prevent freeze-up, it is only necessary to maintain the sample line above 0°C. This can be done using a simple variac and a bimetallic thermometer in the sample line. A given variac setting will correspond to approximately a constant temperature differential between ambient and the sample line. Precise temperature control is unnecessary.

The advisability of keeping the entire sample line above the sample dewpoint will be considered in the section entitled Sample Interaction with the Interface System. In general, this practice is not necessary and is not recommended for a minimum system.

SYSTEM RESPONSE TIME

An important requirement of the sampling system is that its 95% response time must be less than eight minutes. In general, the sampling system can be divided into plug-flow volumes, dead-end volumes, and back-mixing volumes. The overall system response depends on the type and number of these volumes.

Plug-Flow Volumes

A plug-flow volume is one in which the length-to-diameter ratio is large (~ 10 or greater) and through which the gases pass at a relatively high velocity (on the order of feet per second). Examples of plug-flow volumes are sample lines, condenser coils, and tubing connecting the interface components. For plug-flow volumes, axial dispersion can be neglected, and the response time is simply the volume divided by the volumetric flow rate in consistent units [see Equation (1)]. The 95% and 100% response times are the same since it is assumed that axial dispersion is negligible.

When several plug-flow volumes occur in series, the overall system response time is the sum of the response times of the individual volumes. An actual sampling system will contain a combination of both plug-flow and back-mixing volumes. The effect of each plug-flow volume will be to add a constant time increment to the system response equal to its volume divided by its flow rate. The overall response lag of the system due to plug-flow volumes is therefore determined by summing the individual plug-flow volumes and dividing by the volumetric sample flow rate.

Dead-End Volumes

A dead-end volume is a volume which is connected to the mainstream but through which no bulk flow passes. Dead-end volumes can potentially affect the response time of the system. An example of a dead-end volume is the calibration line in Figure I-1. If span gas were flowed through the system before switching to the sample at time zero, calibration gas will diffuse into the sample line creating a potential response lag.

It is possible to calculate the rate of diffusion from calibration line (or from any dead-end volume) to the sample line. This calculation is given in Appendix D for the following situation. At times less than zero, SO_2 span gas is flowed through the calibration line and through the sample line to the analyzer. At time zero sample containing no SO_2 is drawn through the sample line and the calibration line becomes a dead-end volume which is assumed to be infinitely long. The calculation determines the time required for the concentration of SO_2 (leaving the junction of the calibration and sample lines) to drop to 5% of its initial value. For a sample flow rate of 1 SLPM and a 6.35 mm x 1.016 mm calibration line, the 95% response time of the dead-end volume is about 10^{-3} seconds. This value is reasonable since the sample flow rate is so much greater than the diffusive input from the dead-end volume. This result indicates that under all practical conditions, dead-end volumes have a negligible effect on the system response.

Back-Mixing Volumes

A back-mixing volume is one in which the length-to-diameter ratio is small and through which the linear velocity is small. In this case, axial dispersion tends to mix the contents and the simple plug-flow equations are invalid. Examples of mixing volumes are the condensate removal trap, the cell of some analyzers, and the sample pump when piped as shown in Figure I-1. This sample pump arrangement is a mixing volume, since the discharge to suction recirculation is large compared to the input and output from the recirculation loop.

Since all plug-flow volumes can be summed to give an overall system plug-flow volume which adds a constant lag to the instrument response, and since dead-end volumes can be neglected, the remaining mixing volumes can be considered to be connected in series, end-to-end with neglibible transport time between volumes. Then, the overall system response is the response calculated for the required number of sequential mixing volumes plus the time lag due to the plug-flow volumes.

The response characteristics of mixing volumes are treated in detail in Appendix E. The response characteristics of a given volume depend on its time constant, τ:

$$\tau = \frac{V}{F} \tag{3}$$

where τ = time constant (min)
V = volume (liters)
F = actual volumetric flow rate (LPM)

At times less than zero, the concentration is constant at a mole fraction of Y_i in all volumes. At time zero sample containing zero concentration is flowed into the first volume of the sequence. For the special case in which the time constant is the same for each consecutive volume, the response characteristics follow the general equation:

$$\frac{Y_N}{Y_i} = \left(1 + \sum_{n=1}^{N} \frac{t^n}{n!\tau^n}\right) \exp(-t/\tau) \tag{4}$$

where Y_N = mole fraction leaving N^{th} volume
Y_i = initial mole fraction at $t = 0$
N = number of consecutive mixing volumes
t = time
τ = time constant

For the more general case when the time constants are not equal, the results are considerably more complex and do not lend themselves to presentation in generalized form. Equations for one, two, and three consecutive mixing volumes are given in Appendix E.

A sample calculation of system response is shown in Appendix E for the following situation:

Plug-Flow Volume: 60.96 m of sample line and interconnecting tubing of 6.35 OD x 1.016 mm wall.

Back-Mixing Volumes:
Pump and recirculation loop = 200 cm^3
Trap volume = 500 cm^3
Analyzer cell = 400 cm^3

Sample Flow Rate: 1 lPM

The 95% response time calculated for this hypothetical system is 3.28 minutes, 27% of which is due to plug-flow volumes and the remainder to mixing volumes. Response time may be reduced either by increasing the flow rate or reducing the volume. In this respect, it is important not to use greatly oversized components in the sampling interface. In addition, the pump recirculation loop should be kept as small as is practically possible.

If response time problems are encountered in the field tests, the sample flow rate will be increased and the system will be modified to by-pass the excess to vent as shown in Figure I-2. If this contingency proves to be necessary, only enough sample will be by-passed by decrease the system response to the eight minute limit.

PUMP REQUIREMENTS

Diaphragm and bellows pumps are generally conceeded to be superior to other types of pumps for gas sampling, at least wnen positioned upstream of the analyzer. Their primary advantages are:

- they do not require a shaft seal and are therefore not subject to potential failure of the seal and contamination of the sample by air in-leakage;
- they do not require internal lubrication which could contaminate the sample;
- they develop quite adequate suction and discharge heads at flow rates well above those required for sampling systems;
- they are relatively inexpensive.

When the pump is placed downstream of the analyzer, and the sample is "pulled" through the entire system, a simple water on air aspirator can be used. These have a distinct advantage over the diaphragm or bellows pumps in the fact that they have no internal working parts and are, therefore, less prone to failure. However, they require a continuous supply of regulated air, steam, or water which may not always be conveniently available. As pointed out in the subsection entitled Positioning of Sample Pump, systems operating with the pump downstream of the analyzer must make some provision for regulating the pressure (e.g., a pressure regulator or vacuum breaker) at the analyzer. For analyzers with a built-in pressure regulator (e.g., TECO), the air aspirator may be preferrable to mechanical pumps.

When positioned upstream of the analyzer, the sampling pump should be capable of pulling a reasonable vacuum at the suction and providing a reasonable positive pressure at the discharge when operated at the intended sample flow rate. The higher the suction and discharge heads, the longer the system can operate without changing filter elements. In general, high vacuums should be avoided at the suction side, since this increases the possibility of air in-leakage. Minimum specifications for the pump are flexible, but it is advisable to require at least 2 SLPM into 20.68 k N/m^2 at a suction of -13.79 k N/m^2.

Pump performance curves are shown for small diaphragm pumps in Figure I-12. It is apparent that these pumps considerably exceed the minimum specifications (the manufacturer supplies smaller pumps, but at the same cost). For a suction head of -13.79 k N/m^2 (4 in Hg vac.) and a discharge head of 20.68 k N/m^2, the pump delivers about 8.5 SLPM. This is plenty of flow to cover contingency plans for sampling at higher flow rates.

The control of pump discharge pressure and flow rate should be implemented in accordance with the manufacturer's recommendations. The two most common methods of control are a throttle valve on the pump discharge and a by-pass valve from pump discharge to suction (see Figure I-1). The latter method is recommended for diaphragm pumps when operated significantly below the pump curve (i.e., at flow rates considerably below what the pump will deliver at a given suction and discharge head). Severely throttling the discharge causes the pump to work against a much higher discharge pressure and considerably reduces pump life.

When placed upstream of the condensate trap the sampling pump must be capable of passing liquid condensate. The pump should be lcoated above the condensate trap so that condensate can drain away by gravity flow.

Field experience reportedly shows (5) that sampling pumps have a high rate of failure because of corrosion and particulate abrasion. Other factors being equal, pump selection should be based on reliability and maintenance consideration. This requires field-test information for various types of pumps. For the field demonstration portions of this program a diaphragm pump (Thomas Industries) was selected since it is available with completely Teflon-coated internal construction and is more resistant to corrosion than the 316 SS internals of the bellows pump. Problems were encounted during the field demonstration with particulate plugging of the diaphragm pump as described in Part II, page 21 of this report. These problems could probably have been eliminated by positioning the pump as shown in alternative B of Figure I-4 rather than alternative A. Others (37) have also reported problems with diaphragm pumps in sampling applications.

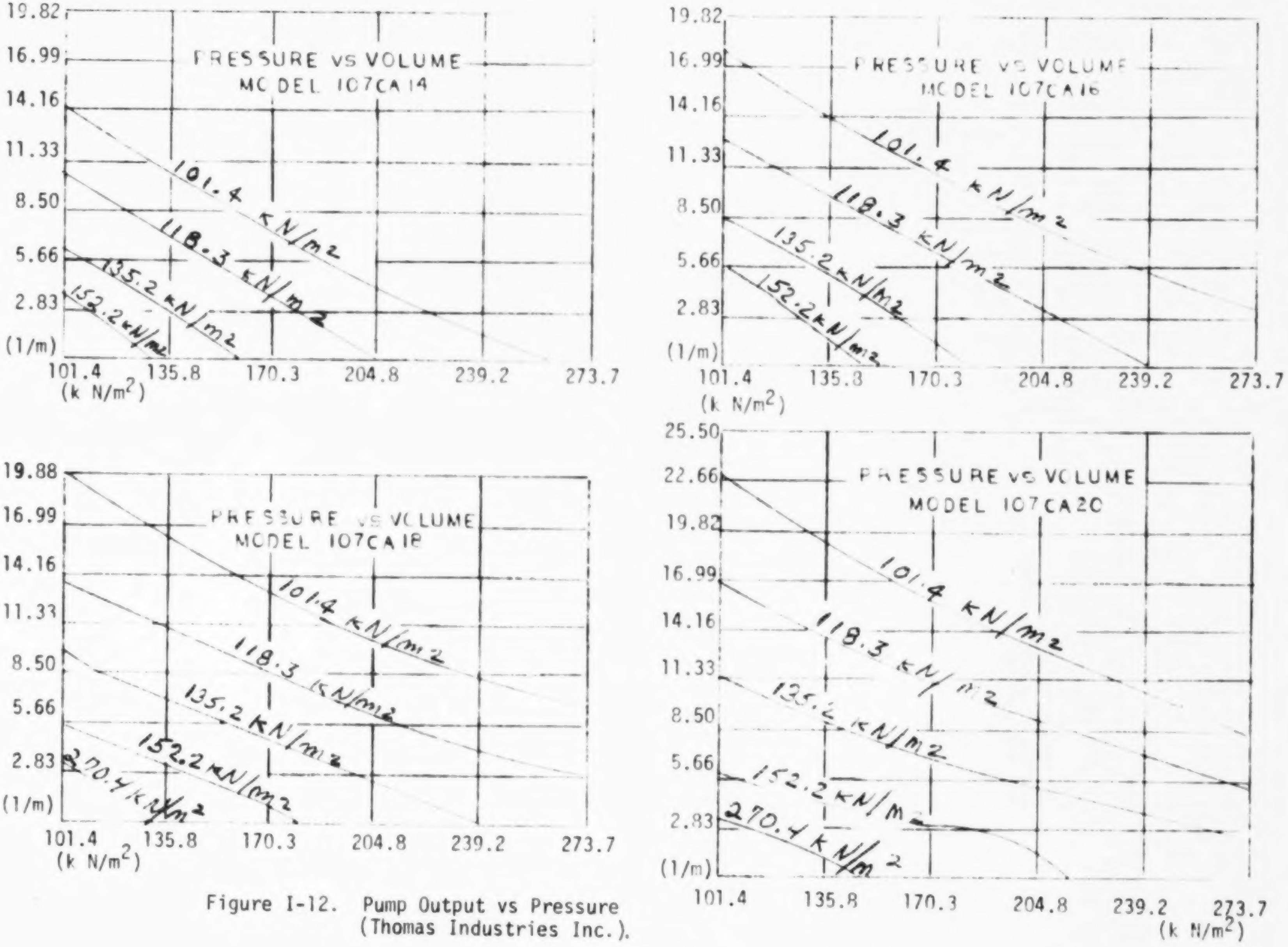


Figure I-12. Pump Output vs Pressure (Thomas Industries Inc.).

MOISTURE REMOVAL

Combustion stack gases contain significant quantities of water vapor which condense out as the sample cools from the stack temperature to room temperature. For some analyzers which are insensitive to water vapor and can operate at high temperatures (e.g., the UV instruments) the problems of moisture removal can be avoided by keeping the temperature of the sample above its dew point. This will, of course, require heated sample lines and heated filters and possibly, depending on placement, a heated pump. Use of a totally heated system appears to be inconsistent with the criteria for a minimum design, but there may be situations in which it achieves an overall cost minimum.

For analyzers which cannot operate at very high temperatures, moisture removal is a necessity. This is most readily accomplished by allowing the sample to cool as it passes through the sample line. It is very important to pitch the sample lines in a downward direction so that condensate drains away from the probe tip toward the condensate trap. It is also advisable to avoid low spots in the line where condensate can collect.

Some commercially available systems maintain the sample above its dew point until it reaches the condenser,at which point it is rapidly cooled. This is done primarily to avoid solubility losses of the species being measured. The advisability of this practice will be considered in the section entitled Sample Interaction with the Interface System.

Some instruments, the NDIR's in particular, are sensitive to water vapor. This sensitivity can be circumvented by one of three methods: (1) the use of optical filtration within the analyzer, (2) removal of all water vapor, or (3) the use of a constant water level in both the sample and calibration gases. The use of optical filtration is a function of analyzer design and will not be considered further.

Substantially all water vapor can be removed by the use of dessicants or permeation dryers. It is of interest to determine the amount of water vapor that must be removed in order to operate within the accuracy limits of ± 10% of span. The effect of water vapor will increase as lower concentrations of SO_2 or NO_x are measured. The measurement of NO_x from a gas fired power plant represents a "worst case" since the typical maximum emission limit is only 127 ppm (Table I-2). A typical water sensitivity for an NDIR instrument is on the order of 100 to 1. That is, 100 ppm water registers as 1 ppm on the analyzer. For this sensitivity the water level must be reduced to 1270 ppm which corresponds to a dew point of -17.78°C.

The use of a constant moisture level in both the sample and calibration gases is the most common method of eliminating the effects of water vapor. This can be done by passing both through a refrigerated condenser controlled at 1.67°C.

Care should be taken not be dry out the condenser by operating for long periods with calibration gases. Under most circumstances this would not be a problem since a flow of dry gas at 2 SLPM would pick up only about 0.6 ml of water per hour at 1.67°C.

Refrigerated Condenser

Refrigerated condensers are available in packaged form (e.g., Hankison Corporation) for cooling sample gas streams. A number of other temperature-regulated cooling devices could be easily modified for use. One particularly interesting possibility, in relation to a minimum design, is the use of a small domestic-type refrigerator containing a cooling coil for the sample and the condensate trap. Lines could be fed into and out of the refrigerator by removing a small piece of molding around the refrigerator door. As pointed out in the subsection entitled Heat Transfer from Sample Lines, a Teflon coil (or other plastic) could be used with only a slight loss in heat transfer rate.

The heat requirements for cooling and drying the sample are very small. As shown in Table I-2 the maximum typical moisture content expected for Category I sources is 16% for a gas-fired power plant. For a sample flow rate of 2 SLPM the cooling requirement is 23 k joule/hr (see Appendix F). This requirement increases in direct proportion to flow rate.

The other quantity of importance in the design of the condenser is the surface area required to cool the gas. This depends to some extent on the internal construction of the condenser. If it is assumed that the condenser is capable of maintaining the outside wall of the cooling coil at 1.7°C, then the coil length is determined by the internal film resistance to heat transfer. In general, the heat transfer rates can be calculated from the information in Appendix C. Enough surface area must be provided to remove the latent heat of vaporization in addition to cooling the gas stream.

Dessicants

Dessicants are inconvenient and expensive for removal of water vapor. Even if used after a refrigerated condenser to remove the remaining 0.68% water vapor, frequent maintenance is necessary. For example, a commercially available Drierite column containing .567 kgm of Drierite and placed at the condenser outlet would last only three days at most. In addition, there is the possibility of interactions with constituents of the sample stream other than water. Some loss of SO_2 on dessicant materials has been observed (6). Therefore, dessicants are not recommended for use in sampling systems.

Permeation Dryers

Permeation dryers (e.g., Perma Pure Products, Inc.) have been used with success (18) in drying stack gases. Stack gases are passed through the tube side of a tube-and-shell-type dryer in which the tubes, made of ion-exchange membranes, selectively pass water but retain other stack gas constituents. The driving force for water permeation is provided by either evacuating the shell side of the dryer or purging the shell side with dry air. The sample must be kept above its dew point since permeation occurs from the gas phase. Thus the sample line must be heat traced up to and including the first 15 cm of the dryer. At flows of 2 to 3 SLPM, water reductions of 2000 to 1 are claimed. Dew points of -18°C and below are routinely obtained.

Several persuasive advantages can be listed for the permeation dryer: (1) materials of construction do not come into contact with liquid condensate and are therefore less prone to corrosion; (2) a condensate trap is not required for removal of liquid; (3) there is no possibility of sample loss by solution in liquid condensate; and (4) it is competitively priced with refrigerated condenser units. The disadvantages are that some problems have been encountered with particulate plugging in field tests on combustion sources, and that the operation of a permeation dryer is somewhat less convenient than the use of a refrigerated condenser. A vacuum pump and controls must be maintained on the shell side of the dryer, or a regulated supply of dry purge air must be used. If the dryer is located in the instrument house the entire sample line must be kept above the sample dew point. If located in the vicinity of the stack, the heat tracing problem is reduced but the accessories and controls (vacuum pump, pressure gauge, flow meter and valve) would be in a less accessible location. Long lines could be run to and from the dryer but these are again inconvenient. Nevertheless, the permeation dryer offers a very interesting alternative, and in many cases, particularly for dust-free stacks, the advantages may be over-riding.

A commercially available refrigerated condenser was selected for the field demonstration according to the following rationale. Some doubt still remains as to whether the permeation dryer is suitable for use on combustion stacks because of particulate plugging. Also, assuming the corrosion rate for the condenser is acceptably slow and the solubility losses are small (see section entitled Sample Interaction with the Interface System) the over-riding advantages for the condenser become its simplicity of operation and the lack of heat traced sample lines held above the sample dew point. The domestic type refrigerator certainly provides the most economical approach in terms of initial investment, but both the time required for modifications and the reliability of its service are questionable.

Removal of Condensate

Condensate can be removed from the sample line by allowing it to collect in a volume or trap while the gas passes on to the analyzer. This trap can be drained manually, as part of a weekly maintenance routine, or automatically. For a flow rate of 2 SLPM the rate of condensate accumulation is about 18 ml per hour (see Appendix F), assuming a total moisture content in the feed of 16%. This amounts to slightly over three liters collected per week. Thus the trap could consist of a simple gallon container that is manually drained each week. The advantages of this alternative are that the trap would be very cheap and simple and would not be prone to mechanical failures. The primary disadvantage is that such a large volume would add considerably to the response time of the system. In addition the trap would be prone to human neglect and possible overflow. However, this alternative may achieve a cost minimum particularly where the stack gases contain less moisture and a smaller trap volume can be used.

A simple device for automatically removing condensate is the ball-float trap, an example of which is shown in Figure I-13. As condensate collects, the float rises, opening the drain valve at the bottom of the trap. Traps of this type are available from steam trap manufacturers but the materials of construction are typically not compatible with the corrosive condensate that must be handled. A number are available with stainless

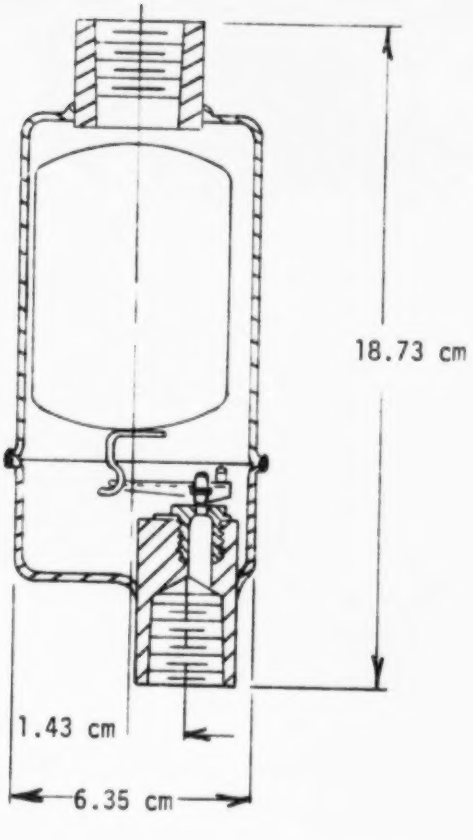

18.73 cm
1.43 cm
6.35 cm

Figure I-13. Ball-Float Trap for Removal of Liquid Condensate (Armstrong Machine Works).

steel working parts but with cast iron or mild steel enclosures. For most of these traps the capacity is much greater than required and some are fairly expensive. Ball-float traps are also manufactured for removal of condensate from compressed air lines, but again the materials of construction are not particularly corrosion resistant. Although an extensive search was not conducted, the ball-float trap of Figure I-13 is the only one found at a reasonable cost that appeared to be suitable for the present application. The potential disadvantage of the ball-float trap is that corrosion and/or particulates may prevent the drain valve from seating properly and thus cause sample loss into the instrument house.

A second alternative for automatically removing condensate is to have an automatically controlled drain valve which is actuated either by a level switch within the trap or by a timer. An external timer is more reliable than inexpensive level switches and less expensive than sophisticated level-detecting devices. A reasonable time cycle can be easily calculated from the sample flow rate, moisture content, and trap volume.

When the trap operates under positive pressure as in alternative A of Figure I-4, condensate is removed simply by opening a valve to atmosphere. When operated under negative pressure as in alternative B of Figure I-4, removal is not so simple. For manual removal, on a weekly basis, the pump could be shut down while the trap is drained, or the trap could be pressurized with compressed air. For automatic removal, a trap with a barometric leg could be used as shown in Figure I-14. For a pump suction of 13.79 k N/m^2 vacuum, a length of 1.4 m would be required for the barometric leg. In fact, if constructed of glass or transparent plastic, the trap could be used to measure the sample line pressure and thereby the pressure drop across the probe-tip filter. This trap has an additional advantage of containing no internal working parts to malfunction. The disadvantage of the barometric trap is that it is not very compact and not very flexible in terms of the operating pressure range. However, contingent plans for the field demonstration include the use of such a trap if alternative B of Figure I-4 is found necessary.

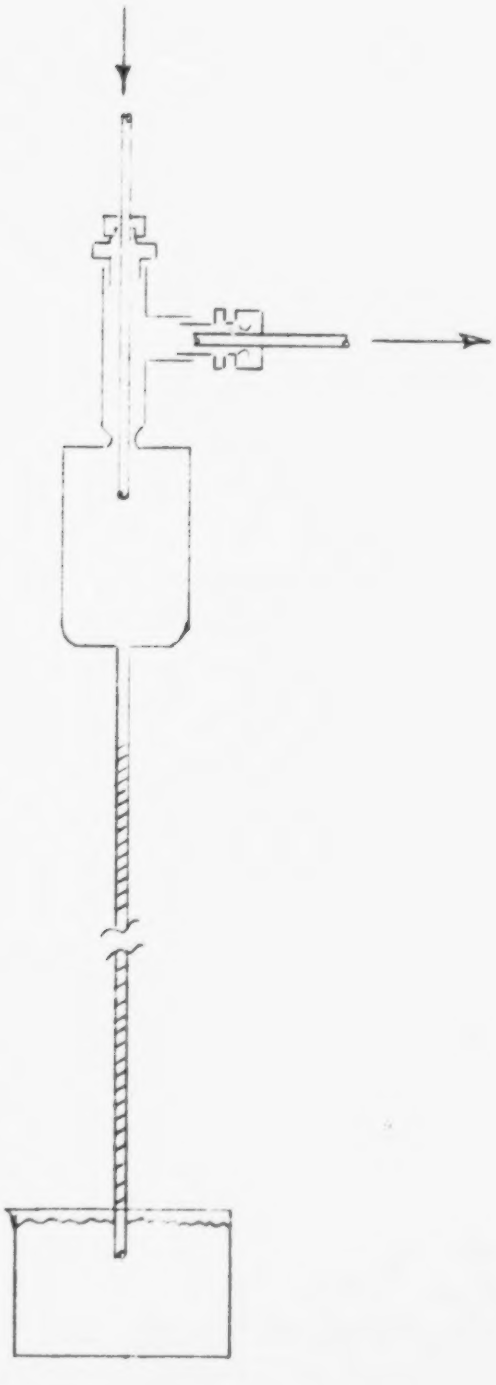


Figure I-14. Condensate Trap Using Barometric Leg.

For traps in which a drain valve is actuated by a level switch or a timer, a solenoid valve must be simultaneously actuated to admit compressed air to the trap forcing the condensate out against atmospheric pressure.

ΔP-ΔT Relation

As pointed out in the subsection entitled Positioning of Sample Pump, moisture removal is a function of the trap temperature and pressure. If the trap is located upstream of the pump and if it operates at the same temperature as other components in the interface, then further condensation can occur when the sample goes through the pump and its pressure is increased. It is a simple matter to calculate the temperature increase required to prevent condensation for a given pressure increase. Figure I-15 shows the required ΔT for a given ΔP below atmospheric. For example, if the trap operates at 25°C and -34.47 k N/m^2 while the analyzer is operating at atmospheric pressure, the analyzer must be operated at 7.2°C above trap temperature or 32.2°C in order to be sure that no condensation will occur in the analyzer.

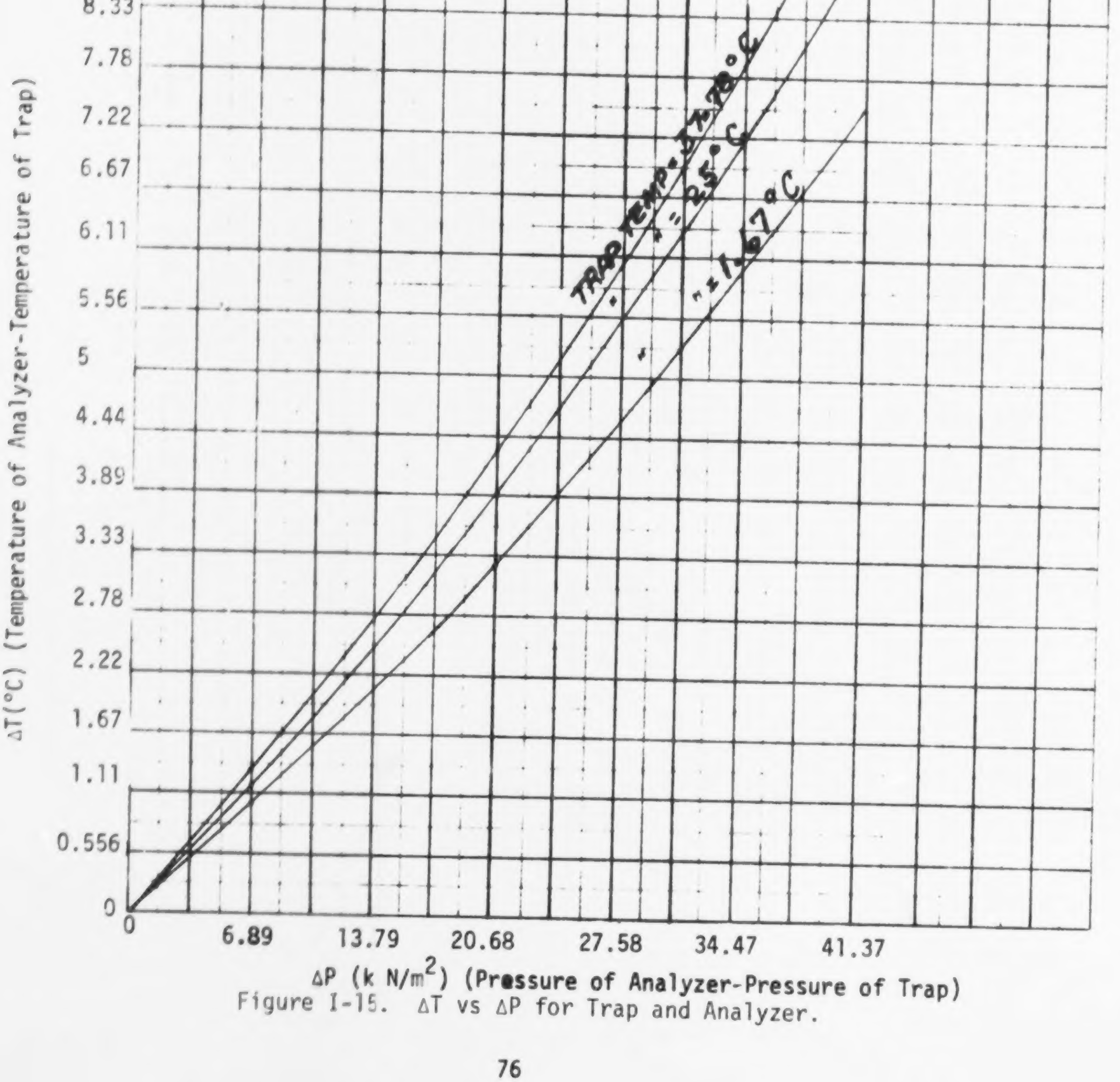


Figure I-15. ΔT vs ΔP for Trap and Analyzer.

Fine Filtration

The particulate removal requirements for the analyzers listed in Table I-5 generally call for substantially complete removal of particles above one micron in size. This is best accomplished by a fine filter in the vicinity of the analyzer. Filters can be divided into two broad categories: surface filters and depth filters.

Surface filters remove particulates by presenting a fine porous structure to the gas streams. These pores prevent the passage of particulates which collect at the surface of the filter element. Examples of surface filter elements are paper, polymer membranes, metal membranes, porous metals and ceramics, etc. Depth filters, on the other hand, collect most of the particulates within the bulk of the filter element. Examples of depth filters are loosly packed fiberous materials and relatively large diameter granular materials.

Surface type filters are best suited for use on dry solid particulates. When a surface layer of these particulates builds up on the filter the increase in pressure drop will not be excessive provided the surface layer remains dry and porous. However, if the surface layer of particulates becomes moist or if the particles are gummy and can coalesce, the filter quickly becomes fouled and the pressure drop becomes excessive. Surface filters when used in gas filtration can generally remove particles smaller than the pore size of the filter element. This is due to electrostatic capture of smaller particles and may result in retention of particles an order of magnitude below the pore size.

Depth filters can be used for gummy solids and for moist gas streams as well as for dry solid particulates. Therefore, they offer the advantage of flexibility in case of a system malfunction. A fine grade depth filter can retain essentially all particulates. Particles larger than about 0.5µm can be captured by direct inertial impact with the filter medium while particles less than about 0.5µm exhibit Brownian motion which greatly increases their chances of collision with and retention by the filter medium. Large particles are held by mechanical forces while small particles are retained by van der Waals forces.

There are a number of commercially available surface filters and depth filters that can be supplied with housings compatible with the corrosive nature of the sample stream (see subsection entitled Sources of Sampling System Components). These can be obtained in porosities that will efficiently remove particles well below one micron in size.

Efficient filtration can be obtained by using a tube packed with fine glass wool. Glass wool packing will function as a depth filter although, depending on the packing density, larger particles may accumulate primarily at the surface. A glass tube holder is preferable since the conditions of the filter media can be checked visually. Construction details for gas sampling filters made of glass wool and other materials have been given (14), but for flow rates considerably greater than required for continous monitoring. A packing density of 0.08g/cm^3 was recommended with a bed depth of two inches and a linear flow rate, based on the filter cross sectional area, of less than .61 m/sec. It is important to make sure the glass fibers lie normal to the direction of gas flow, as far as possible, to prevent channelling. It may be necessary to use some trial and error in packing the filter to the proper density. Commercially available filters have an advantage in reliability, reproducibility, and convenience. Nevertheless, a glass tube filled with glass wool will be used for the field demonstration because of its obvious cost advantage.

INSTRUMENTATION

As a general rule, instrumentation should be kept as simple as possible on all equipment intended for operation by plant personnel. This is particularly true for a minimum system.

It is necessary to measure the flow rate of sample to each analyzer, but as pointed out in the subsection entitled Control of Sample Flow Rate, it is usually unnecessary to accurately control the flow rate. Small rotameters of 10 to 20% accuracy are quite sufficient to give an indication of flow. Some analyzers will have a built-in sample flow meter obviating the need for any flow instrumentation in the interface.

There are two points at which temperature indication may be helpful: (1) at the cold end of a heated sample line to make sure the temperature remains above freezing, and (2) at the refrigerated condenser to set the desired control temperature. Temperature can be simply and effectively measured by using a bimetallic dial thermometer inserted into the sample line through one branch in a tee.

Pressure measurement at the pump suction is useful for determining the pressure drop across the probe tip filter and sample line. This indicates when the filter element needs to be changed or when the sample line is becoming plugged. This pressure measurement is not really essential if the filter is a high-loading type which requires infrequent maintenance.

Pressure measurement at the pump discharge is useful for two purposes: measuring the pressure drop across the fine filter and adjusting the recirculation through the pump bypass to keep the discharge pressure low. Without this pressure check, the pump could be run at high pressure/low flow conditions which shortens pump life.

SPECIFIC SOURCE/ANALYZER COMBINATIONS

Previous sections have presented general design considerations based on the source/analyzer combinations of Figure I-1. The conditioning requirements for other combinations are generally less demanding. This section considers separately the requirements for monitoring power plants, nitric acid plants, and sulfuric acid plants in relation to the four types of analyzers listed in Table I-5.

Power Plants

The basic sampling system components required for monitoring combustion sources are:

- Probe tip filter (for particles $\sim$ 10 μm and greater)
- Sample pump
- Refrigerated condenser (NDIR instruments only)
- Condensate trap
- Fine filter (may not be required for UV instruments depending on pore size of coarse filter at stack)

These components have been discussed in detail in preceding sections.

Sulfuric Acid Plants

The exact nature of the sampling interface for sulfuric acid plants depends to some extent on the type of emission control process that is used. As shown in Table I-4, typical SO_2 concentrations in uncontrolled plants are an order of magnitude above the emission limit. If a dual-absorption process is used to reduce SO_2 emissions, the stack gases are dry and moisture removal components are unnecessary; however, acid mist must be removed. If a wet scrubber is used to reduce SO_2, acid mist removal is unnecessary, but water vapor must be removed or controlled at a fixed level for NDIR instruments.

The basic components required for sampling dry sulfuric acid stack gases are:

- Probe tip (no filter required)
- Demister
- Sample pump
- Fine filter

When off-gases from a wet scrubber are monitored, the basic interface components are:

- Probe tip (no filter required)
- Sample pump
- Refrigerated condenser (NDIR instruments only)
- Condensate trap
- Fine filter

It may not be necessary to provide automatic condensate withdrawal when sampling off-gases from a wet scrubber. If the gases are assumed to be saturated at 37.8°C, cooling to 25°C, for analysis of a sample flowing at 1 slpm (only one analyzer must be fed), will produce only 270 ml of condensate per week. This could be handled in a relatively small volume on a weekly maintenance basis.

Of the interface components required for SO_2 stack sampling, the demister is the only one that remains to be considered in detail. The simplest demister is a large settling volume in which the gas velocity is low and liquid particles can settle by gravity. This is effective for removing large particles but is ineffective, under practical conditions, for removing smaller particles. For example, the terminal velocity (29) of a 100 μm particle of specific gravity 1.5 is about .3048 m/sec. For a sample flow rate of 2 slpm, 100 μm particles will settle out in a 1.27 cm diameter tube. However, 10 μm particles have a terminal velocity of .3 cm/sec and a 12.7 cm diameter tube is required for removal.

Cyclone separators can be used to demist the sample by centrifugal force. However, these may be expensive and prove to be too large to obtain efficient operation with the small flow rates used in sampling.

The third type of demister is an impingement separator. When an obstruction is placed in the path of the gas flow, the gas is easily diverted, but liquid droplets are carried forward by their momentum, impinge on the surface, and are collected. The most commonly used industrial separator of this type is the wire mesh demister. The same effect can be achieved by using glass fibers or Teflon fibers which are more corrosion resistant.

Taking the typical emission limit of Table I-4 for sulfuric acid mist and assuming isokinetic sampling at a rate of 1 slpm, the rate of sulfuric acid mist collection is only 0.27 grams per week. Even at the much higher "uncontrolled" emission rate of .131 mg/sl, only 1.3 grams of mist are collected per week. Therefore, it is unnecessary to continuously remove acid mist condensate from the system. This can be done manually on a monthly or even semi-annual basis.

The demister to be demonstrated in field tests combines both gravity separation and impingement on glass wool as shown in Figure 16. It is constructed of ordinary PVC pipe fittings and should be simple and inexpensive to fabricate.

Nitric Acid Plants

The sampling of stack gases from nitric acid plants may require special handling to prevent NO_2 solubility losses. Sample interactions with the interface system will be considered in detail in the section entitled Sample Interaction with the Interface System. It is sufficient for present purposes to indicate that significant NO_2 losses can occur by dissolution in the stack gas condensate.

It is obvious from Table I-3 that nitric acid plants must use some type of waste gas treatment to reduce NO_x output. The two most common types of waste gas treatment are catalytic reduction and wet scrubbing with water or caustic. For catalytic treatment, a typical water vapor concentration of about 4% can be expected, and for scrubbers, the stack gases will be saturated at the scrubber temperature. Thus condensation can be expected for both types

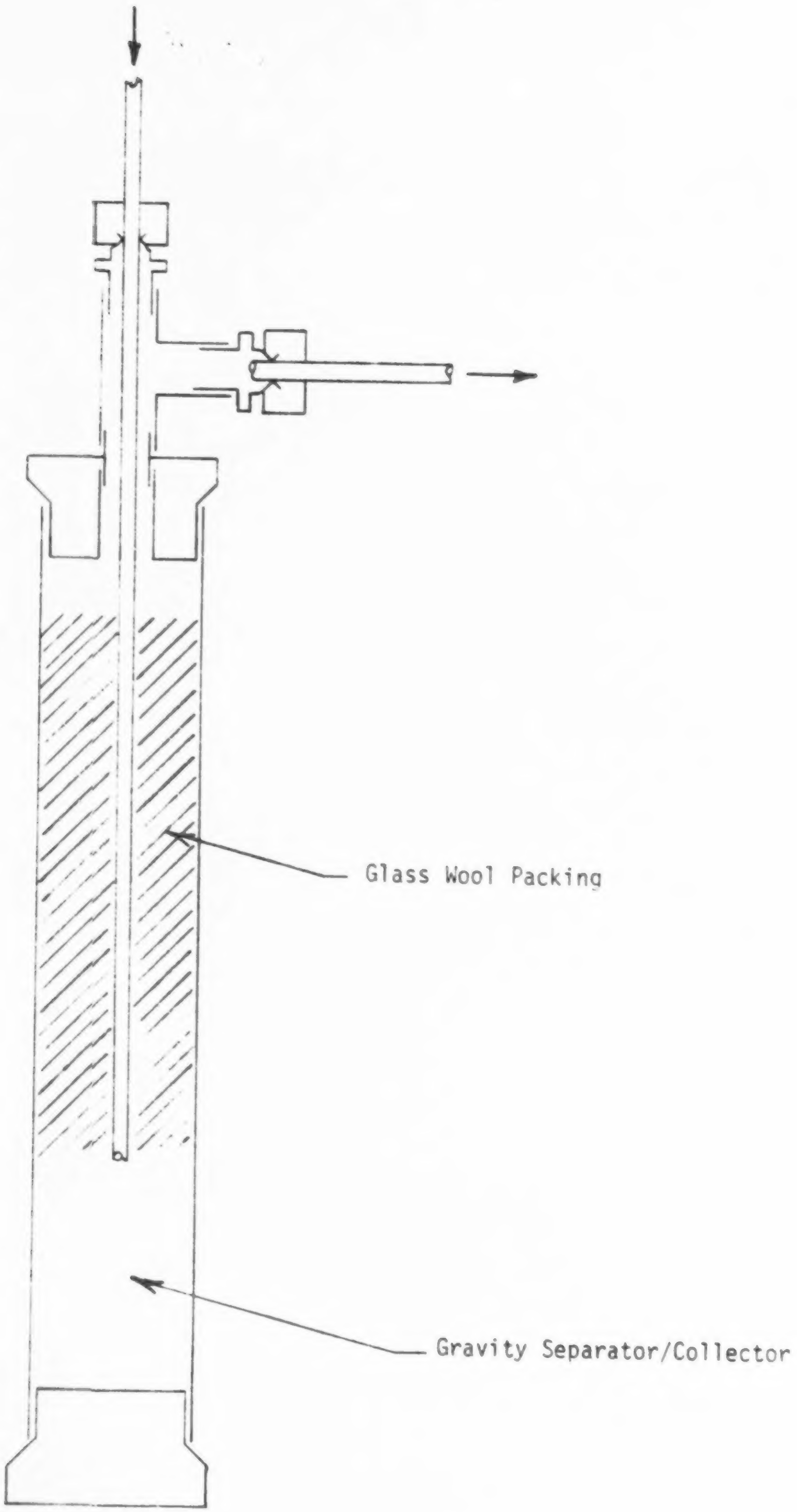

Glass Wool Packing
Gravity Separator/Collector

Figure I-16. Gravity and Glass Wool Demister.

of waste gas treatment when the sample is cooled to room temperature. Furthermore, it appears from the few data (16, pp. 24 and 25) located on NO_2 emissions, that NO_2 can be a significant fraction of the total NO_x for both types of waste gas treatment.

Solubility losses of NO_2 can be prevented by one of two means: 1) the entire interface can be heat traced to keep the sample above its dew point, and 2) a permeation dryer can be used to selectively remove water vapor while retaining other gases. It is again difficult, in the absence of operating experience with these two alternatives, to choose the one which represents an overall cost minimum. Complete heat tracing is unacceptable for the NDIR instruments, which are sensitive to water vapor, and for the Aerochem instrument which cannot tolerate dewpoints above 21°C. Heat tracing may also be unacceptable for the other chemiluminescent and electrochemical analyzers if the dewpoint is above their maximum allowable sample temperature (Table 5). Heating tracing is, of course, a viable alternative for the UV instruments.

Permeation drying, on the other hand, can be used with all instruments and may represent a cost minimum even for the UV analyzers. The sampling interface components required are:

- Probe tip (without filter)
- Permeation dryer (with accessories)
- Sample pump
- Fine filter

NDIR Analyzers

The distinguishing feature of NDIR analyzers is their sensitivity to water vapor. As pointed out in the subsection entitled Moisture Removal, this requires either removal to a dewpoint of below -17.8°C or maintenance of a constant moisture level in both the sample and calibration gases.

UV Analyzers

The distinguishing feature of UV analyzers is their high operating temperature and the manufacturers' recommendation that the sample be kept above its dewpoint. This mode of operation is really only required when NO_2 solubility losses are to be prevented, and significant NO_2 concentrations are encountered only in nitric acid stack gases. For other applications, the higher cost of a completely heat traced interface, as compared to a room temperature condensate trap, does not appear to be justified, at least in the short run.

Another noteworthy feature of the UV analyzers is their higher tolerance of particulates. If sufficient removal is obtained in coarse filtration, fine filtration is not required.

Chemiluminescent Analyzers

There are no particularly noteworthy requirements of the electrochemical analyzers.

Electrochemical Analyzers

The chemiluminescent analyzers are unique in the fact that they must have some means, internal to the instrument itself, to control the flow rate of sample to the reaction chamber. The TECO instrument provides internal pressure regulation and the Aerochem instrument provides internal flow regulation. For either instrument, it is advisable to follow the interface design recommended by the manufacturer. For example, the TECO instrument draws sample through the interface and analyzer using a pump on the downstream side of the analyzer.

The internal pressure regulator maintains the pressure at about -17 k N/m^2 vacuum. Therefore, there is no option in the placement of the pump. A pump is typically supplied with both the TECO and Aerochem instruments. Other design variables such as particulate removal, moisture removal, sample line materials, etc., can be specified as previously discussed. For both instruments, moisture can be removed by a room temperature trap provided the analyzer is kept above room temperature.

SOURCES OF SAMPLING SYSTEM COMPONENTS

One of the problems faced in implementing an interface design is locating manufacturers of suitable components. There are a number of components that can be fabricated without problem, but in many cases the cost of labor for fabrication makes it less expensive to buy commercially available components. It should be emphasized that our survey of sampling system components was by no means exhaustive. There may be many other manufacturers whose products are acceptable or even preferable over the ones listed in this section. Furthermore, specific field experience has not been obtained for most of the components listed. Nevertheless, manufacturers of products which appear to have potential for sampling systems are listed in Appendix H. A number of these listings are taken from Reference 30.

INTERFACE FOR FIELD DEMONSTRATION

The major interface design considerations have been presented in previous sections. Some of the more mundane details of construction can be best obtained by an examination of the engineering specifications for a specific system. Appendix G gives the specifications for an interface using an NDIR and an electrochemical analyzer on power plant stacks.

SAMPLE INTERACTION WITH THE INTERFACE SYSTEM

Regardless of the exact design of the sampling interface, it is essential that the sample be transported from stack to analyzer with tolerable losses and interactions. There are several mechanisms by which interaction can occur, including:

- reaction;
- absorption;
- adsorption; and
- dilution.

Dilution can occur by air leakage into portions of the system which are under vacuum. Its importance is primarily a function of the quality of fabrication rather than design, and will not be considered further.

REACTIONS

Gas phase species can be lost both by homogeneous gas phase reaction and by heterogeneous catalytic reaction on system components or collected particulates. Reaction losses will be examined for each of the three species of interest, viz., SO_2, NO, and NO_2.

SO_2 Losses

Catalytic oxidation of SO_2 to SO_3 is the most likely means of SO_2 loss by reaction. Reaction will occur only when the gases are at a high temperature, i.e., at the probe-tip filter of combustion sources. Materials of construction, such as stainless steel, Teflon, glass, and ceramics, are generally very poor catalysts and would not be expected to catalyze the reaction. However, particulates collected at the probe-tip filter could conceivably be catalytically active, although this is unlikely. To check the magnitude of potential SO_2 losses, it is assumed that the alundum thimble is loaded to capacity with 71 grams of fly ash, and that the fly ash has the same catalytic activity as a good commercial SO_2 oxidation catalyst (platinum or alumina). Assuming a sampling rate of 2 SLPM and a stack concentration of 1000 ppm SO_2, the space velocity through the fly ash is 7.54×10^{-5} g-moles SO_2/(hr) (gram fly ash). Kinetic data are shown in Figure 17 (31) for a commercial SO_2 oxidation catalyst and a reaction mixture of 1000 ppm SO_2 and 0 ppm SO_3. Since the reaction rate is proportional to $P_{SO_2}^{1}$ and $P_{SO_3}^{-0.5}$, this rate curve represents a severe case. When the data is extrapolated to a reasonable sampling temperature (204.4°C), the reaction rate is 1×10^{-6} g-moles SO_2/(hr) (g-catalyst), this rate would give only a 1.3% loss of the SO_2 in the sample. Since the reaction rate is directly proportional to the partial pressure of SO_2 the same percentage loss would be incurred by more dilute samples. It is therefore concluded that catalytic loss of SO_2 will be negligible under all practical sampling conditions.

This conclusion was verified experimentally by loading a stainless steel filter element with 7 grams of fly ash and sampling 1200 ppm SO_2 in air at a flow rate of 1 SLPM. This corresponds to a space velocity of 4.59×10^{-4} g-moles SO_2/(hr) (g-fly ash). No measurable loss of SO_2 was observed for operating temperatures of 21.1°C, 204.4°C, and 371.1°C, as determined by shunting the sample through a "clean" filter.

NO Losses

The oxidation of NO to NO_2 is a very interesting reaction:

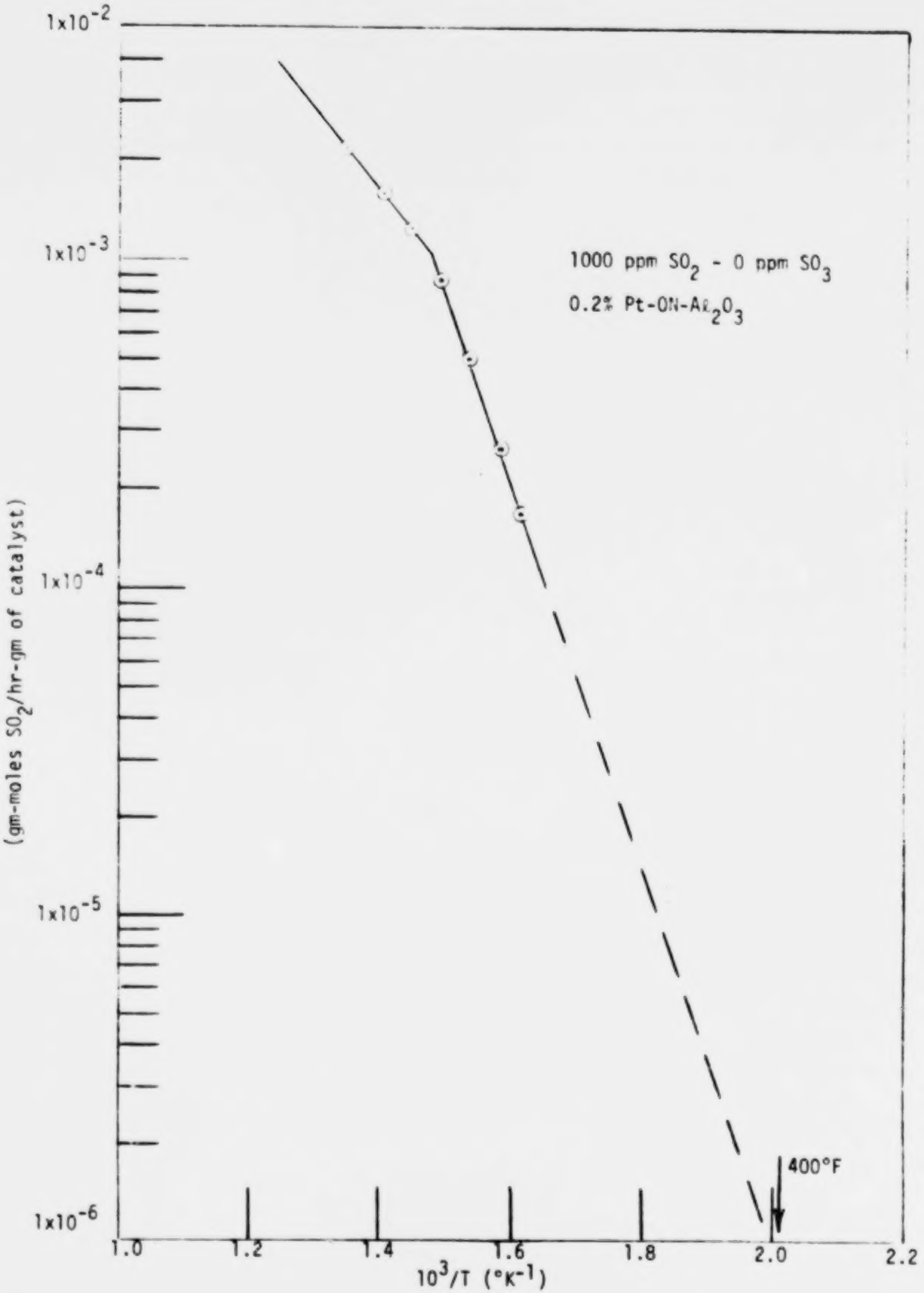
$$2\ NO + O_2 \rightleftarrows 2\ NO_2$$

It is one of the few examples of a third-order homogeneous reaction. That is, two molecules of NO and one molecule of O_2 must simultaneously collide before reaction can occur. The rate of oxidation is:

$$-\frac{d\,P_{NO}}{dt} = k_1\,P_{NO}^{2}\,P_{O_2} - k_2\,P_{NO_2}^{2} \qquad (5)$$

The rate of oxidation is proportional to the square of the NO partial pressure so that the rate decreases greatly at low NO concentrations. The other interesting fact concerning the oxidation is that the rate constant k_1 decreases as the temperature increases, which is opposite to the typical temperature dependence of rate constants. From

Figure I-17. Reaction Rate Data for SO_2 Oxidation.



Equation (5), the rate of oxidation is a maximum when the partial pressure of NO_2 is zero. Assuming $P_{O_2} >> P_{NO}$, then P_{O_2} is approximately constant. Equation (5) integrates to:

$$\frac{(P_{NO})_o}{P_{NO}} = 1 + k_1 \, (P_{NO})_o \, P_{O_2} \, t$$

where

$(P_{NO})_o$ = Initial partial pressure of NO

P_{NO} = Partial pressure of NO at time t

P_{O_2} = Partial pressure of O_2

k_1 = Forward rate constant

For a "worst case" analysis, an average sample line temperature of 40°F is assumed. At this temperature, k_1 is about 32.5 atm^{-2} sec^{-1} (32). From Table I-2, the typical maximum NO_x limit is about 500 ppm and the oxygen partial pressure is about 0.03 atm. The time required for a 10% conversion of NO to NO_2 at these conditions is 3.80 min. Thus, the average residence time for the sampling system must be less than 3.8 min. Average residence time is determined by dividing the system volume by the flow rate. For a flow rate of 1 SLPM, a system volume of 3.8 liters is required for a 3.8 min. residence time. For most sampling systems, this requirement is easily met. For example, 60.96 m of 6.35 OD x 1.016 mm tubing contains a volume of 0.893 liters. This leaves approximately 3 liters for other system components.

The conversion of NO to NO_2 does not really represent a loss, since the emission limit is set on NO_x, and one mole of NO_2 is produced for each mole of NO reacted. However, it will be shown later that conversion to NO_2 will increase solubility losses. Nevertheless, the above calculations show that, under practical sampling conditions, the loss of NO by reaction (and subsequent absorption) will not exceed the 10% tolerance limit.

The possibility of catalytic oxidation of NO to NO_2 on fly ash collected in the probe-tip filter was checked experimentally. No loss was observed when flue gas doped with NO was passed through a filter containing fly ash. The control equipment was run with a clean filter. The sampling temperature was 232.2°C; NO concentration, 1300 ppm; and Q/M, 42 SLPM/gram fly ash.

NO_2 Losses

Nitrogen dioxide can be reduced to NO and N_2 as in the catalytic process for treatment of waste gas from nitric acid manufacture. However, this requires a catalyst, high temperature, and a reducing atmosphere. While the first two requirements may be met for combustion stack gases, the use of excess air in combustion rules out the possibility of a reducing atmosphere in the stack. Therefore, loss of NO_2 is not expected. Furthermore, combustion stack gases typically contain only less than 5% of total nitrogen oxides (36) in the NO_2 form. Thus, NO_2 losses can be safely neglected.

ABSORPTION

Absorption of gas phase species by components of the interface does not generally represent a loss mechanism. The interface component must eventually become saturated, at which point the true steady-state concentration is measured by the analyzer. This type of interaction may cause a response lag and will be considered in the following section.

Sample loss may occur by solution of gas phase species in condensate, which is collected and removed from the system. Maximum losses will occur when the gas comes to equilibrium with the condensate at the point of removal.

SO_2 Solubility Losses

The vapor-liquid equilibria involved in the solution of SO_2 in water are considered in detail in Appendix I (33). Losses are determined for condensate removal at 25°C from a sample stream containing 6% water vapor and various SO_2 concentrations. As shown in Table I-2, 6% moisture is typical of coal-fired and oil-fired power plants (SO_2 monitoring is not required for gas-fired power plants). The results of Appendix I indicate no significant loss of SO_2 at levels above 10 ppm. In fact, at levels of about 10 ppm SO_2 and higher, the SO_2 partial pressure leaving the condenser is actually greater. This is due to the fact that the reduction in gas phase volume caused by removal of water vapor outweighs the solubility loss of SO_2.

Solubility losses of SO_2 were measured experimentally in the test system shown in Figure I-18. The impinger was filled with deionized water, and the test gas, containing 1200 ppm SO_2, was metered through the impinger at a flow rate of 3.3 slpm. The gas then passed through a 15.2 m coil of polyethylene tubing, a water trap, and an SO_2 analyzer.

The analyzer response along with the impinger water temperature and coil inlet and outlet temperatures is plotted vs experiment time in Figure I-19. Initially, it takes about 20 minutes to saturate the water in the impinger at 20-25°C. At saturation, a steady-state SO_2 concentration of 1160 ppm is measured. The temperature of the impinger is then increased

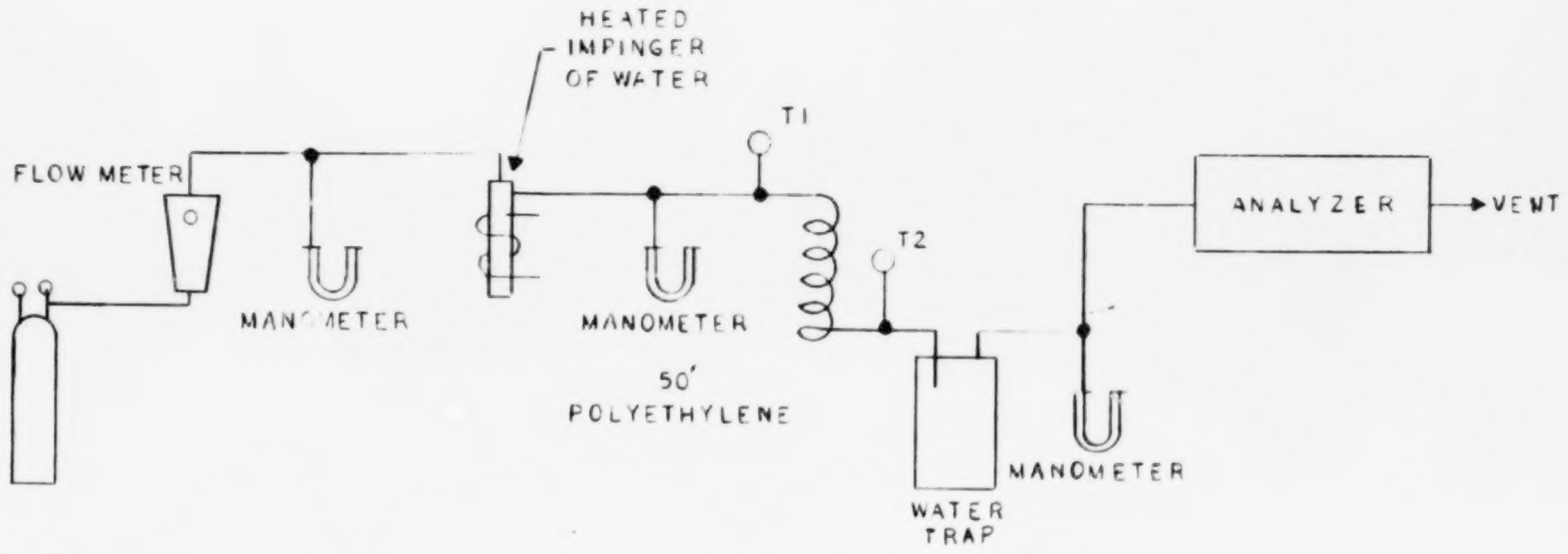

HEATED IMPINGER OF WATER
T1
FLOW METER
ANALYZER
VENT
T2
MANOMETER
MANOMETER
50'
POLYETHYLENE
MANOMETER
WATER TRAP

Figure I-18. Experimental Apparatus for Solubility Loss Tests.

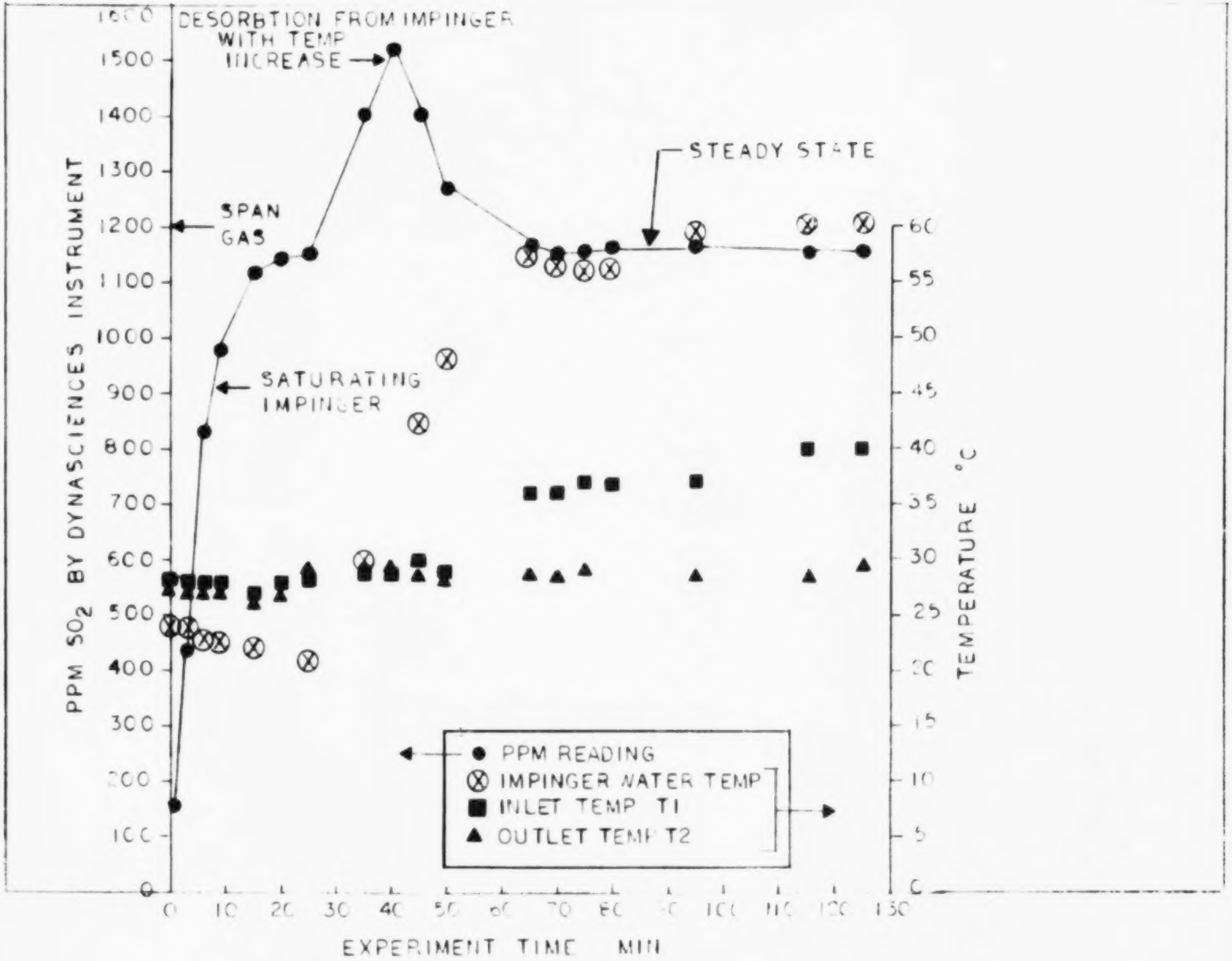


Figure I-19. Measured SO_2 Level and Temperature Conditions.

from 20°C to 60°C. This increases the amount of water vapor in the sample gas from 2.3% to 20%. If SO_2 solubility losses are important, more SO_2 should be removed in the water trap and a lower steady-state SO_2 concentration should be measured. As shown in Figure I-19 when the impinger temperature is increased SO_2 desorbs, but as the impinger is held at 60°C the steady-state SO_2 concentration approaches the same value, 1160 ppm. This indicates that there is no significant loss of SO_2 in the water trap.

It may also be noted that the reason the SO_2 reading never reaches 1200 ppm is that the 1200 ppm is for dry span gas while the gas passing through the analyzer is saturated with water vapor at the trap temperature. Taking the dewpoint at the analyzer as 25°C, then the vapor pressure in the sample stream is $\sim 3.07 \text{ k N/m}^2$ and the span gas is diluted to:

$$\frac{1200 \text{ ppm}}{1 + \frac{23 \text{ mm Hg}}{760 \text{ mm Hg}}} = 1160 \text{ ppm}$$

which is exactly what was measured.

NO Solubility Losses

The solubility of nitric oxide is less than sulfur dioxide, and NO follows Henry's Law. At 0°C the relation between liquid mole fraction, X, and partial pressure, P_{NO}, is (34):

$$X_{NO} = P_{NO}/H = 1.923 \times 10^{-5} P_{NO}$$

where P_{NO} is in atmospheres. The solubility is less at higher temperatures. A simple calculation for 10% water vapor indicates a solubility loss of only 0.0002% on a dry basis. Therefore, NO solubility losses are entirely negligible.

NO_2 Absorption Losses

The absorption of NO_2 by water proceeds by the following reaction:

$$3NO_2(g) + H_2O(\ell) \rightleftarrows 2HNO_3(\text{sol'n}) + NO(g)$$

Absorption presumably takes place through the intermediate formation of nitrous acid, but equilibrium concentrations of nitrous acid are small and the overall reaction is as given above. There is considerable disagreement on equilibrium data (32) as well as rate data (35) for the NO_2-water system.

The equilibrium data indicate that the uptake of NO_2 can be very great. Concentrated solutions of HNO_3 can be easily formed by absorption of NO_2. Essentially all NO_2 will be absorbed under practical equilibrium conditions.

Loss of NO_2 can be avoided if the rate of approach to equilibrium is sufficiently slow. The rate of NO_2 absorption is given in Appendix J. It is assumed that the entire inside surface area of the tube is wetted with condensate. For a sample flow rate of 2 slpm through 6.35 mm o.d. x 1.016 mm wall tubing, 50% of the sample is lost in only one foot of tubing. For unheated sample lines of any practical length, complete loss of NO_2 can be expected.

A number of commercially available sampling systems keep the sample above its dewpoint until it reaches the condenser. It is then rapidly cooled to prevent solubility losses. The effectiveness of this procedure depends in large part on the condenser design. An ordinary 6.35 mm diameter coil of tubing in 1.67°C surroundings would require at least a foot length to cool 2 slpm of flow. A more elaborate design would have to be devised in order to prevent significant NO_2 losses.

An attempt was made to experimentally measure NO_2 losses by the following procedure. NO_2 was doped into flue gas at a rate sufficient to give 500 ppm at the sampling point downstream. The flow setting was determined by doping with NO to give a 500 ppm concentration and using the same setting for NO_2. The experimental precision was not very good because of problems with flow stabilization. However, when doping with NO_2, an NO_x concentration of 350 ppm was measured rather than 500 ppm, and more than 70% of the NO_x was in the NO form. This indicates a significant NO_2 loss.

Loss of SO_2 and NO by reaction and absorption have been shown to be negligible under practical sampling conditions. The absorptive loss of NO_2 represents the only real problem. However, the samll concentration of NO_2 in combustion stack gases would allow the interface to completely remove NO_2 and still remain within the 10% tolerance limit on NO_x. Stack gases from nitric acid manufacture may contain significant amounts of NO_2. For this case, a permeation dryer is recommended to remove water vapor without removing NO_2. Other alternatives are to keep the sample above its dewpoint from stack to analyzer, or, if feasible, to use heated sample lines and a low residence time condenser.

ADSORPTION

Adsorption of gas species onto interface components does not affect the steady-state concentration measured at the analyzer but may result in an unacceptably long response time. Adsorption interactions are best determined experimentally since they are difficult to quantify theoretically.

Tests were conducted with both NO and SO_2 using 15.2 m lengths of six different sample line materials. Nitrogen containing 1200 ppm of either NO or SO_2 was passed through the selected sample line, and the concentration was measured and recorded as a function of time. At time zero, the sample flow was discontinued, and room air was passed through the sampling system at the same flow rate (1 slpm). The system response to room air was measured for each sample line.

The results are shown in Figure I-20. Desorption from sample line walls results in a tailing effect and longer response times. The wall effects can be compared more easily by determining the time from the point where the concentration first begins to fall to the point at which it reaches 5% of the initial value. The response times for SO_2 are given in Table I-12. The "blank" gives the response time of the system without sample lines. Teflon, polypropylene, and 316 SS are all quite close to the "blank" response and therefore exhibit negligible adsorption effects. Nylon exhibits a slightly longer response time indicating a small adsorption effect. Polyethylene and tygon give response times which are, respectively, three

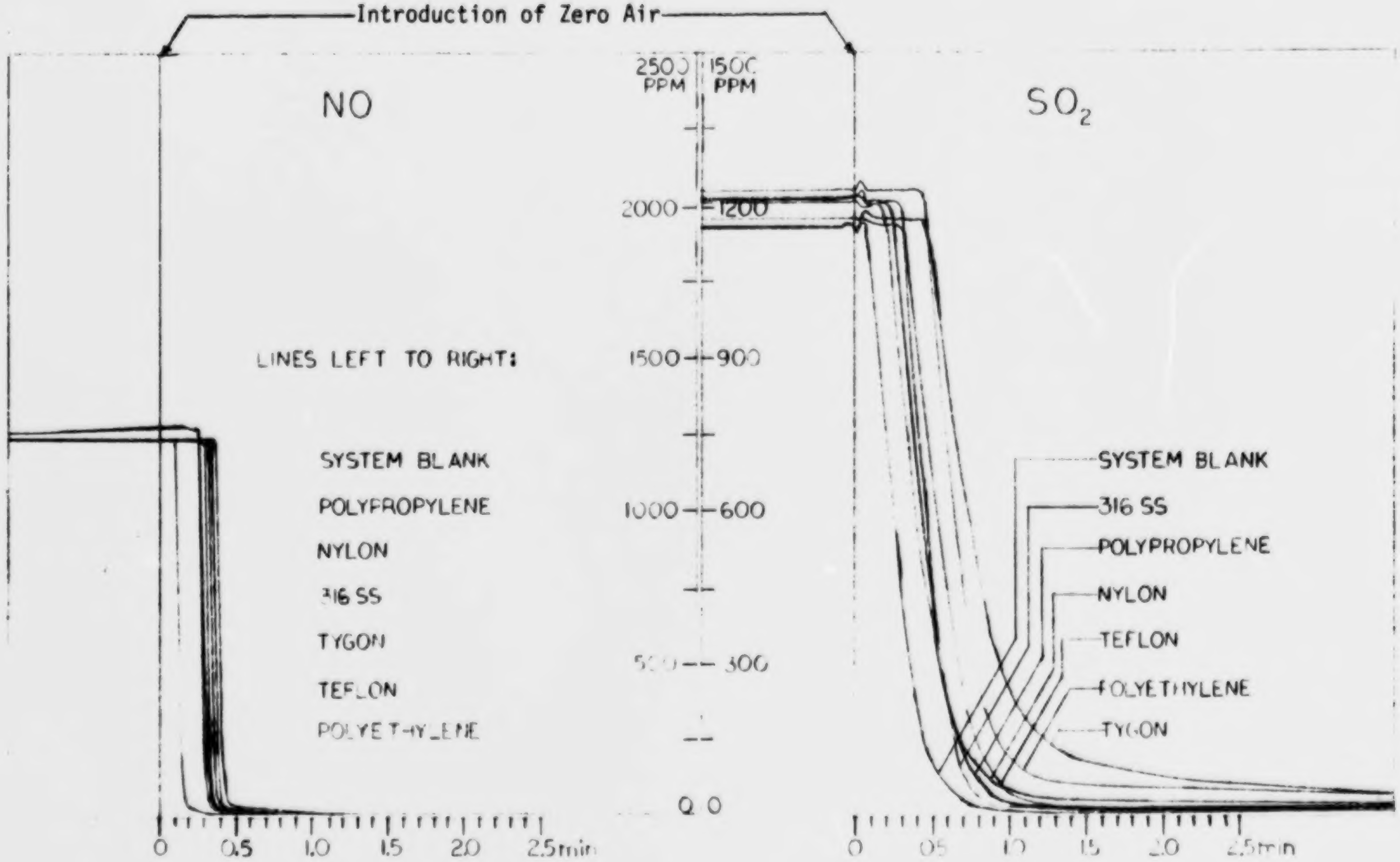


Figure I-20. Adsorptive Interactions with Various Sample Line Materials.

Table I-12

RESPONSE TIMES FOR VARIOUS SAMPLING LINE MATERIALS

Material	Size	95% Response Time for SO_2[*] (min)
Blank	No sample line	0.54
316 SS	6.35 x 0.889 x 15.24 m	0.44
Polypropylene	6.35 x 0.762 x 15.24 m	0.62
Teflon	9.525 od. x 6.35 i.d. x 15.24 m	0.63
Nylon	6.35 x 0.762 x 15.24 m	0.75
Polyethylene	9.525 o.d. x 6.35 i.d. x 15.24 m	1.58
Tygon	11.113 o.d. x 6.35 i.d. x 15.24 m	2.05

---

[*] Measured from first observed concentration change to 5% of initial concentration

and four times the "blank" response. Adsorption effects for these materials are therefore significant. Hence, polyethylene and tygon are not recommended for extensive use in SO_2 monitoring systems.

The results for NO indicate that none of the materials tested exhibit significant adsorption effects with this gas. Therefore, for NO monitoring any of the materials tested can be used.

Based on the above results and the results of the section entitled Design of Sampling Interface, subsection Materials of Construction, polypropylene appears to be the material that is most suitable from the standpoint of a minimum design. Its chemical resistance is satisfactory for all except concentrated sulfuric and nitric acids; its adsorptive interactions are negligible; and it is very inexpensive.

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APPENDIX A

CALCULATION OF STACK GAS COMPOSITIONS

The approximate composition of combustion stack gases can be easily calculated from the composition of the fuel and from the amount of air used for combustion. The use of 20% excess air will be assumed throughout.

A. NATURAL GAS

For gas-fired power plants, the composition of Texarkana natural gas was assumed (19):

$$CH_4 = 96\%\ \text{vol}$$

$$N_2 = 3.2\%$$

$$CO_2 = 0.8\%$$

The heat of combustion for methane (20) is 37.73 k joule/l, and the combustion reaction is:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Basis: 2832 sl of fuel

$$\text{Theoretical } O_2 = .96(2832)(2) = 5437.4 \text{ sl } O_2$$

$$\text{Theoretical air} = 5437.4/0.21 = 25893 \text{ sl air}$$

$$\text{Actual air} = 25893 + (0.20)(25893) = 31070 \text{ sl air}$$

$$N_2 \text{ in stack} = (0.79)(31070) = 24545 \text{ sl } N_2$$

$$O_2 \text{ in stack} = (0.20)(0.21)(25893) = 1087.5 \text{ sl } O_2$$

$$CO_2 \text{ in stack} = 2718.7 \text{ sl } CO_2$$

$$H_2O \text{ in stack} = (.96)(2832)(2) = 5437.4 \text{ sl } H_2O$$

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The stack gas composition is:

Constituent	sl	%
CO_2	2741.4	8.09
H_2O	5437.4	16.04
N_2	24636.0	72.67
O_2	1087.5	3.20
TOTAL	33902.3	

$$\text{Flue gas volume} = \frac{33{,}902.3 \text{ sl}}{2832 \text{ sl fuel}} \times \frac{1 \text{ sl fuel}}{37.73(0.96) \text{ k joules}} \times \frac{10^6}{10^6} = \frac{330.5 \text{ skl}}{\text{G-joule}}$$

$$\text{Fed } NO_x \text{ limit} = \frac{86. \text{ gm}}{\text{G-joule}} \times \frac{22.4 \text{ l}}{46 \text{ gm}} \times \frac{1 \text{ G-joule}}{330{,}500 \text{ sl}} = 1.27 \times 10^{-4} = 127 \text{ ppm}$$

$$\text{Fed particulate limit} = \frac{43 \text{ gm}}{\text{G-joule}} \times \frac{1 \text{ G-joule}}{330{,}500 \text{ sl}} \times \frac{1000 \text{ mg}}{\text{gm}} = 0.13 \text{ mg/sl}$$

B. FUEL OIL

The approximate composition of residual fuel oil (3) is:

C = 86% wt

H = 10%

H_2O = 1%

N = 0.5%

S = 1.6%

Inerts = 0.9%

The heating value (3) is 42.5 k joule/gm. The combustion reactions are:

$$C + O_2 \rightarrow CO_2$$

$$4H + O_2 \rightarrow 2H_2O$$

$$2N \rightarrow N_2$$

$$S + O_2 \rightarrow SO_2$$

Basis: 45.36 kg of fuel

Constituent	kg	g-moles	g-moles O_2 Required
C	39.04	3250.9	3250.9
H	4.536	4536	1134
H_2O	4.536	24.95	
N	.227	16.33	
S	.726	22.68	22.68
			4407.6

Theoretical O_2 = 4407.6 g-moles

Theoretical air = 4407.6/0.21 = 20988.6 g-moles air

Actual air = 20988.6 + (0.20)(20988.6) = 25186.3 g-moles air

N_2 to stack = (0.79)(25186.3) = 19897.2 g-moles N_2

O_2 to stack = (0.20)(0.21)(20988.6) = 881.5 g-moles O_2

The stack gas composition is:

Constituent	g-moles	%
CO_2	3250.9	12.33
H_2O	2292.9	8.70
N_2	19912.6	75.54
O_2	881.3	3.34
SO_2	22.68	0.086
	26360.4	

$$\text{Flue gas volume} = \frac{26360.4 \text{ g-moles}}{45360 \text{ g}} \times \frac{22.4 \text{ sl}}{1 \text{ g-mole}} \times \frac{1 \text{ gm}}{42.5 \text{ k joule}} \times \frac{10^6}{10^6}$$

$$= 306 \text{ skl/G-joule}$$

$$\text{Fed } SO_2 \text{ limit} = \frac{344 \text{ gm } SO_2}{\text{G-joule}} \times \frac{22.4 \text{ sl}}{64 \text{ gm}} \times \frac{1 \text{ G-joule}}{306{,}000 \text{ sl}} = 3.94 \times 10^{-4} = 394 \text{ ppm}$$

$$\text{Fed } NO_x \text{ limit} = \frac{129 \text{ gm } NO_2}{1 \text{ G-joule}} \times \frac{22.4 \text{ sl}}{46 \text{ gm}} \times \frac{1 \text{ G-joule}}{306{,}000 \text{ sl}} = 2.05 \times 10^{-4} = 205 \text{ ppm}$$

$$\text{Fed particulate limit} = \frac{43 \text{ gm}}{\text{G-joule}} = \frac{1 \text{ G-joule}}{306{,}000 \text{ sl}} \times \frac{1000 \text{ mg}}{\text{gm}} = \text{C}.14 \text{ mg/sl}$$

C. COAL

The composition of Pittsburgh coal is assumed (21):

C = 76.6% wt

H = 5.2%

O = 6.2%

S = 1.3%

N = 1.6%

Ash = 9.1%

The heating value is 31.65 kjoule/gm (21). The combustion reactions are:

$$C + O_2 \rightarrow CO_2$$

$$4H + O_2 \rightarrow 2H_2O$$

$$S + O_2 \rightarrow SO_2$$

Basis: 100 lb fuel

Constituent	kg	g-moles	g-moles O_2 Required
C	34.746	2895.3	2895.3
H	2.359	2358.7	589.7
O	2.812	175.8	-88.0
S	0.590	18.4	18.4
N	0.726	51.7	
			3415.4

Theoretical O_2 = 3415.4 g-moles O_2

Theoretical air = 3415.4/0.21 = 16,263.8 g-moles air

Actual Air = 16,263.8 + 0.20 (16,263.8) = 19,516.6 g-moles air

N_2 to Stack = (0.79)(19,516.6) = 15,418.1 g-moles N_2

O_2 to Stack = (0.21) (0.20) (16,263.8) = 683.1 g-moles O_2

The stack gas composition is:

Constituent	g-moles	%
CO_2	2895.3	14.32
H_2O	1179.3	5.83
N_2	15447.9	76.38
O_2	683.1	3.38
SO_2	18.4	0.09
	20224.0	

$$\text{Flue Gas Volume} = \frac{20224\ \text{g-moles}}{45359\ \text{gm fuel}} \times \frac{1\ \text{gm fuel}}{31.65\ \text{kjoule}} \times \frac{22.4\ \text{sl}}{1\ \text{g-mole}} \times \frac{10^6}{10^6} = 315.6\ \text{skl/G-joule}$$

$$\text{Fed } SO_2 \text{ Limit} = \frac{516\ \text{gm } SO_2}{\text{G-joule}} \times \frac{22.4\ \text{sl}}{64\ \text{gm}} \times \frac{1\ \text{G-joule}}{315{,}600\ \text{sl}} = 5.72 \times 10^{-4} = 572\ \text{ppm}$$

$$\text{Fed } NO_x \text{ Limit} = \frac{301\ \text{gm } NO_2}{\text{G-joule}} \times \frac{22.4\ \text{sl}}{46\ \text{gm}} \times \frac{1\ \text{G-joule}}{315{,}600\ \text{sl}} = 4.64 \times 10^{-4} = 464\ \text{ppm}$$

$$\text{Fed Particulates limit} = \frac{43.\text{gm}}{\text{G-joule}} \times \frac{1\ \text{G-joule}}{315{,}600\ \text{sl}} = 1.36 \times 10^{-4}\ \text{gm/sl} = 13.6\ \text{mg/l}$$

APPENDIX B

CALCULATION OF FLOW RATE VS PRESSURE DROP

When the pressure drop is less than about 10% of the downstream pressure and when flow is laminar, the pressure drop through a circular tube is given by the Poiseuille equation (22):

$$P_2 - P_1 = \frac{\mu L \overline{V}}{D^2} \qquad (1)$$

where: μ = absolute viscosity (kg/m-sec)
L = length of tube (m)
$\overline{V}$ = average linear velocity (m/sec)
D = inside diameter of tube (m)
P_2 = upstream pressure (N/m^2)
P_1 = downstream pressure (N/m^2)

The following assumptions are made:

(1) The gas temperature is 25°C along the entire length of tubing. Heat transfer calculations show that the sample quickly comes to the temperature of the surroundings.

(2) For the purpose of calculating fluid properties, the average pressure is taken as 1 atm, and the sample is assumed to be air.

(3) Flow is assumed to be laminar (an assumption which will be checked).

(4) The pressure drop is assumed to be less than 10% of the downstream pressure (which can be checked by the results).

For air at 1 atm and 25°C:

$$\mu = 1.838 \times 10^{-5} \text{ kg/m-sec.}$$

$$\rho = \frac{28.9 \times 10^{-3} \text{kg}}{0.0224 \text{ m}^3} \times \frac{273}{298} = 1.18 \frac{\text{kg}}{\text{m}^3}$$

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The volumetric flow rate is given by:

$$F = \bar{V} S$$

Where: F = volumetric flow rate (l/sec)
S = cross sectional area (m^2)
$\bar{V}$ = average linear velocity (m/sec)

For a flow rate, F_S, given in standard liters per minute, the average linear velocity is:

$$V = 1.667 \times 10^{-5} \frac{F_S}{D^2} \text{ m/sec} \quad (2)$$

Substitution into Equation (1) with L = 30.48 m gives:

$$P_2 - P_1 = 9.356 \times 10^{-9} \frac{F_S}{D^4} \text{ N/m}^2$$

where F_S is the sample flow in standard liters/minute and D is the inside line diameter in m. For the diameter given in cm, D', the corresponding equation is:

$$P_2 - P_1 = 9.356 \times 10^{-17} \frac{F_S}{(D')^4} \text{ N/m}^2$$

This equation was used to calculate the results presented in Figure I-11.

The assumption of laminar flow can be checked by calculating the Reynolds number:

$$Re = \frac{D \bar{V} \rho}{\mu}$$

Or, substituting Equation (2):

$$Re = \frac{1.667 \times 10^{-5} F_S \rho}{\mu D}$$

The higher F_S/D, the higher the Reynolds number. For the range of variables covered in Figure 11, the maximum F_S/D occurs at 100 slpm through .1143 m i.d. tubing.

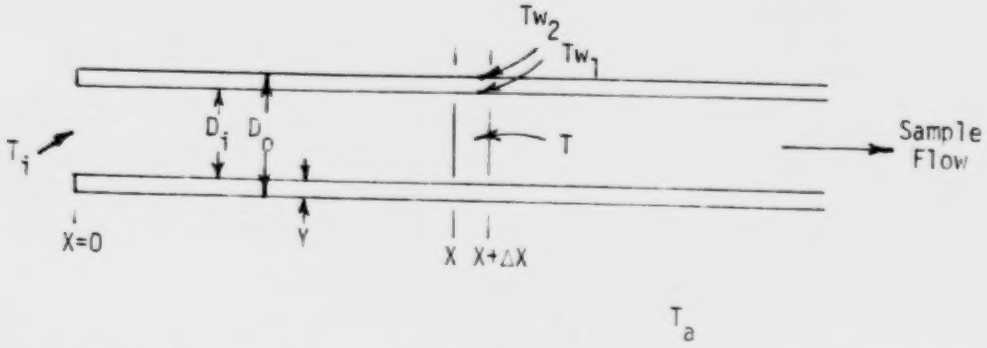
$$Re = 1303$$

The onset of turbulence does not occur until a Reynolds number of 2100 is reached.

APPENDIX C

HEAT TRANSFER FROM SAMPLE LINES

A. DERIVATION OF EQUATIONS



The temperature of the sample gas, T, can be determined as a function of position, X, in the sample line by making a heat balance on a differential segment of line between X and X + ΔX. The rate of heat flow through the walls of the segment is given by:

$$\frac{dq}{dA_o} = U_o\,(T - T_a) \tag{1}$$

where: q = local rate of heat transfer (kjoules/hr)

A_o = outside tube diameter (m^2)

U_o = local overall heat transfer coefficient based on the outside tube diameter

T = average bulk gas temperature within the differential element

T_a = ambient temperature distant from the tube

The heat balance then becomes:

$$\text{Heat Input} = W\,C_p\,T|_X$$

$$\text{Heat Output} = W\,C_p\,T|_{X+\Delta X} + U_o\,\pi\,D_o\,\Delta X(T - T_a)|_{X+\frac{\Delta X}{2}}$$

$$\text{Accumulation} = 0 \text{ (steady state)}$$

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where: W = mass flow rate of sample (kg/hr)
C_p = heat capacity of sample (kjoule/kg-°C)
$T|_X$ = average gas temperature at X (°C)
$T|_{X+\Delta X}$ = average gas temperature at X + ΔX (°C)
D_o = outside tube diameter (m)

These terms lead to the following differential equation:

$$- W C_p \frac{dT}{dX} = U_o \pi D_o (T - T_a) \qquad (2)$$

In general, C_p depends on the gas temperature which varies along the length of the tube and U_o also depends on linear position or, more directly, on the temperature of the tube wall. C_p is assumed constant at the average sample gas temperature over the length of the tube and U_o is also assumed constant at an average temperature. With these assumptions, Equation (2) can be integrated between 0 and X, T_i and T to give:

$$\ln \frac{T_i - T_a}{T - T_a} = \frac{\pi D_o U_o}{W C_p} X \qquad (3)$$

where T_i is the sample gas temperature at the tube inlet. This is the equation used to calculate sample gas temperature as a function of position.

B. DETERMINATION OF HEAT TRANSFER COEFFICIENTS

Of the various quantities needed to calculate a numerical value from Equation (3), U_o is the most difficult to obtain accurately. There are three series resistances to heat transfer: from the sample gas to the tube wall, across the tube wall, and from the outside wall to ambient. The overall resistance (reciprocal of the overall coefficient) is equal to the sum of individual resistances (23):

$$\frac{1}{U_o} = \frac{D_o}{h_i D_i} + \frac{Y D_o}{k \bar{D}} + \frac{1}{h_o} \qquad (4)$$

where: h_i = heat transfer coefficient from sample gas to tube wall based on inside diameter (kjoule/hr-m^2-°C)

h_o = heat transfer coefficient from outside tube wall to ambient based on outside diameter (kjoule/hr-m^2-°C)

k = thermal conductivity of tube wall material (kjoule/hr-m-°C)

D_i = inside wall diameter (m)

Y = wall thickness (m)

$\overline{D}$ = average tube diameter, $\frac{1}{2}(D_i + D_o)$ (m)

It remains to determine h_i and h_o.

As shown in Appendix B, flow within the sample lines is laminar under all reasonable sampling conditions, i.e., the Reynolds number is less than 2100. The average Nusselt number from 0 to X for laminar flow inside tubes is given by (24):

$$\overline{Nu} = 3.65 + \frac{0.0668\ (D_i/X)\ Re\ Pr}{1 + 0.04\ [(D_i/X)\ Re\ Pr]^{2/3}} \tag{5}$$

where the dimensionless numbers are:

$$\text{Average Nusselt number} = \overline{Nu} = \frac{h_i\ D_i}{k}$$

$$\text{Reynolds number} = Re = \frac{D_i\ \overline{V}\ \rho}{\mu}$$

$$\text{Prandtl number} = Pr = \frac{C_p\ \mu}{k}$$

and where: k = thermal conductivity of sample gas (kjoule/hr-m-°C)

$\overline{V}$ = average linear velocity (m/sec)

ρ = density of sample gas (kg/m^3)

μ = viscosity of sample gas (kg/m-sec)

Under all practical sampling conditions the second term of Equation (5), which gives the entrance effects at small X, is entirely negligible. The average Nusselt number is then constant at 3.65. This value is actually based on a constant wall temperature along the length of the tube. However, it should not be greatly affected by a varying wall temperature along the sample line length.

Heat transfer from the outside tube wall takes place by natural convection and depends on the Grashof and Prandtl numbers. The Nusselt number at a particular X location averaged over the circumference of the tube is (25):

$$Nu = \frac{h_o D_o}{k} = 0.539 \frac{Pr^{1/2} Gr^{1/4}}{(0.952 + Pr)^{1/4}} \tag{6}$$

The Prandtl number for gases is very insensitive to temperature. For air the Prandtl number varies from 0.70 to only 0.68 over the temperature range of 65.56°C to 326.7°C. Using the value of 0.70 in Equation (6) gives:

$$Nu = \frac{h_o D_o}{k} = 0.40 \, Gr^{1/4} \tag{7}$$

The Grashof number is given by:

$$Gr = \frac{D_o^3 \rho_f^2 \beta_f g \Delta T_o}{\mu_f^2} \tag{8}$$

where: ρ_f = density of air at mean film temperature (kg/m^3)

β_f = coefficient of thermal expansion at mean film temperature = reciprocal of absolute temperature for ideal gases (°k)

g = acceleration of gravity = 9.80 m/sec^2

μ_f = viscosity of air at mean film temperature (kg/m-sec)

ΔT_o = average difference in temperature between outside pipe wall and air distant from tube (°C)

Properties are determined at the mean film temperature which is the arithmetic average of the ambient temperature and the wall temperature at position X. Since the wall temperature is not constant along the length of the sample line, the Grashof number will vary and the Nusselt number will also vary. It is not a simple matter to account for this changing wall temperature. One approach is to assume a constant Grashof number over short lengths of the sample line and to make a calculation for each segment. A more approximate approach is to assume a constant Grashof number despite the variation in wall temperature. The latter approach will be followed.

C. CALCULATION OF TUBING LENGTH FOR COOLING TO 200°F

Plastic materials such as polypropylene cannot be placed directly in the stack of combustion sources because of their heat limitations (approximately 93.33°C). It is of interest to determine the length of heat resistant material (e.g., stainless steel) that must be used before a transition to lower temperature plastics can be made.

The following conditions are used:

D_o = 6.35 mm
D_i = 4.318 mm
F = 2 st. liters/min
T_a = 37.78°C
T_i = 260°C
T_o = 93.33°C (outlet temperature from heat resistant tube)
Sample - air
Tube - stainless steel

The arithmetic average temperature of the sample flowing through the tube is 176.7°C. At the point where the gas sample is at a temperature of 176.7°C the outside wall temperature may be determined as follows. Due to the high thermal conductivity of the tube, assume that the inside and outside wall temperatures are the same. The inside resistance to heat flow is $1/h_i\ D_i$ and the outside resistance is $1/h_o\ D_o$. The temperature of the tube wall will be intermediate between 176.6°C and 25°C and will be determined by the relative magnitudes of the inside and outside resistance. That is, the inside temperature drop is proportional to the inside resistance, etc.

$$\frac{T - T_w}{T_w - T_a} = \frac{1/h_i\ D_i}{1/h_o\ D_o} = \frac{h_o\ D_o}{h_i\ D_i}$$

As a first approximation, $h_o\ D_o/h_i\ D_i = 0.5$ is assumed and T_w = 130.56°C. The average film temperature outside the sample line is 1/2 (130.56 + 37.78) = 84.16°C.

The following properties were determined for air at 84.16°C and 1 atm pressure:

$$\rho = 0.980 \text{ kg/m}^3$$
$$\beta = 1/357.8°\text{k} = 2.795 \times 10^{-3} \text{ °K}^{-1}$$
$$\mu = 2.107 \times 10^{-5} \text{ kg/m-sec}$$
$$\Delta T_o = (84.16 - 37.78) = 46.38°\text{C}$$
$$k = 0.11 \text{ kjoule/hr-m-°C}$$

$$Gr = \frac{(6.350 \times 10^{-3}\text{m})^3 \left(0.980 \frac{\text{kg}}{\text{m}^3}\right)^2 \left(\frac{2.795 \times 10^{-3}}{°\text{K}}\right)\left(9.8 \frac{\text{m}}{\text{sec}^2}\right) 46.38°\text{C}}{(2.107 \times 10^{-5} \text{ kg/m-sec})^2} = 709$$

Substituting in Equation (7) gives:

$$Nu = \frac{h_o D_o}{K} = 2.06 ,$$

and

$$h_c = \frac{(2.06)\ (0.11)}{(6.35 \times 10^{-3})} = 35.75$$

For flow inside the sample tube, fluid properties are calculated at the average temperature 176.7°C.

$$k = .1334 \text{ kjoule/hr-m-°C}$$

$$C_p = 1.0205 \text{ kjoule/kg-°C}$$

The inside heat transfer coefficient is:

$$\overline{Nu} = \frac{h_i\ D_i}{k} = 3.65$$

$$h_i = \frac{(3.65)\ (.1334)}{(4.318 \times 10^{-3})} = 112.76 \text{ kjoule/hr-m}^2\text{-°C}$$

The actual value of $h_o\ D_o/h_i\ D_i$ is 0.47, close to the assumed value of 0.50.

The overall heat transfer coefficient is calculated from Equation (4), taking the thermal conductivity of stainless steel as 39.346 kjoule/hr-m-°C.

$$\frac{1}{U_o} = \frac{6.35 \times 10^{-3}}{(112.76)\ (4.318 \times 10^{-3})} + \frac{(1.016 \times 10^{-3})(6.35 \times 10^{-3})}{(39.346)(5.334 \times 10^{-3})} + \frac{1}{35.75}$$

$$U_o = 24.36 \text{ kjoule/hr-m}^2\text{-}°\text{C}$$

For a flow of 2 slpm

$$W = \frac{2\ \ell}{\text{min}} \times \frac{28.9\ \text{gm}}{22.4\ \ell} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{1\ \text{kg}}{1000\ \text{gm}} = .1548\ \text{kg/hr}$$

Substituting in Equation (3) gives:

$$L = \frac{W\ C_p}{\pi\ D_o\ U_o}\ \ell n\ \frac{T_i - T_a}{T_o - T_a}$$

$$L = \frac{(.1548)\ (1.0205)}{(\pi)\ (6.35 \times 10^{-3})\ (24.36)}\ \ell n\ \frac{260 - 37.78}{93.33 - 37.78} = .45\ \text{m}$$

Therefore, in a length of about .5 m, stack gases at an initial temperature of 260°C would be cooled to the point where low temperature plastics could be used for the rest of the sample line. This calculation is conservative on the basis that a 37.78°C ambient is assumed and a stagnant air mass is assumed.

D. LENGTH REQUIREMENT FOR UNHEATED SAMPLE LINES

A closely related calculation to the previous one is a determination of the maximum allowable sample-line length before condensate freeze-up can be expected in subfreezing surroundings. In order to make a conservative estimate in this case a different set of assumptions must be made. It is assumed that the ambient temperature is -6.67°C and a continuous 16.09 kph wind is blowing normal to the sample line.

It is assumed as a first approximation that the resistance to heat transfer is approximately the same inside and outside the tube. The tube wall will then be at a temperature midway between the sample gas and the ambient. The Reynolds number outside the tube is:

$$Re = \frac{D_o\ \overline{V}\ \rho}{\mu}$$

Properties are determined at the mean film temperature. The mean sample gas temperature is 1/2 (260 + 0) = 130°C. The average wall temperature is 1/2 (130 - 6.667) = 61.67°C. The average film temperature is 1/2 (61.67 - 6.67) = 27.5°C. At this temperature

ρ = 1.177 kg/m^3
μ = 1.847 x 10^{-5} kg/m-sec
k = 0.0944 kjoule/hr-m-°C

The linear velocity corresponding to 16.09 kph is 4.48 m/sec.

$$Re = \frac{(6.35 \times 10^{-3})\ (4.48)\ (1.77)}{1.847 \times 10^{-5}} = 1813$$

For the range of Reynolds numbers between 1 and 4000, the Nusselt number is given by (26):

$$Nu = \frac{h_o\ D_o}{k} = 0.43 + 0.48\ (Re)^{0.5}$$

$$Nu = 20.87$$

or

$$h_o = \frac{(20.87)\ (0.0944)}{(6.35 \times 10^{-3})} = 310 \text{ kjoule/hr-m}^2\text{-°C}$$

For the internal heat transfer coefficient, the average sample temperature is 130°C at which temperature the thermal conductivity of air is 0.1219 kjoule/hr-ft-°C, and the heat capacity is 1.0205 kjoule/kg-°C.

$$\overline{Nu} = \frac{h_i\ D_i}{k} = 3.65$$

$$h_i = \frac{(3.65)\ (.1219)}{4.318 \times 10^{-3}} = 103.04\ \frac{\text{kjoule}}{\text{hr-m}^2\text{-°C}}$$

By Equation (4):

$$U_o = 57.02 \text{ kjoule/hr-m}^2\text{-°C}$$

and from Equation (3):

$$L = \frac{(.1548)\ (1.0205)}{(\pi)\ (6.35 \times 10^{-3})\ (57.02)} \ \ell n \ \frac{260 - 0}{0 + 6.667} = 0.508 \text{ m}$$

Therefore, at a sampling rate of 2 slpm through a 6.35 mm o.d. tube freeze-up may occur within 0.51m.

E. CALCULATION OF TUBE WALL RESISTANCE

It is of interest to calculate the magnitude of the terms making up the overall heat transfer coefficient. From Equation (4), the ratio of wall resistance to internal film resistance is given by:

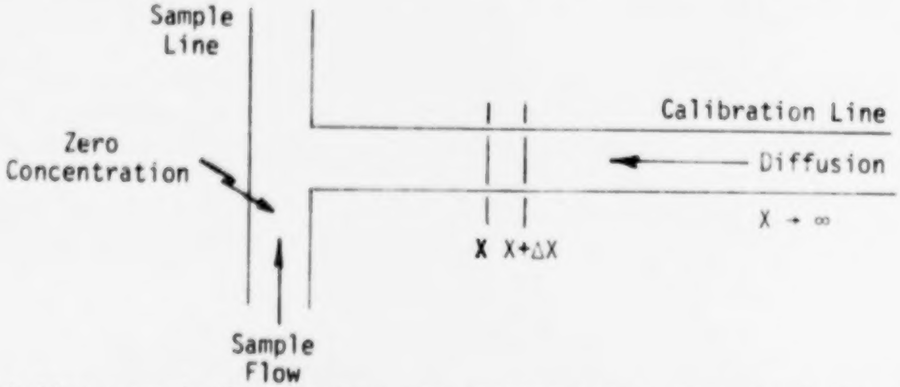
$$\frac{\text{wall resistance}}{\text{internal film resistance}} = \frac{Y\ D_o/k\ \bar{D}}{D_o/h_i\ D_i}$$

For the conditions of the two previous calculations, this ratio is approximately 1.5×10^{-3}. Thus, the resistance due to the stainless steel wall is only about 0.15% of the internal film resistance. If teflon were used for the tube wall at a thermal conductivity of 0.872 kjoule/hr-m-°C, the resistance of the wall would be only about 10% of the internal film resistance. Thus, the tube material has relatively little effect on the rate of heat transfer.

APPENDIX D

EFFECT OF DEAD-END VOLUMES ON RESPONSE TIME

The effect of dead-end volumes will be illustrated by calculating the rate of diffusion of span gas (SO_2) from a calibration line of infinite length into the sample line. In the diagram shown below the concentration at time zero is C_1, the span gas concentration, throughout the calibration line, and is zero, the sample concentration, throughout the sample line. At times greater than zero, diffusion of span gas into the sample occurs. The diffusive flux is given by Fick's Law (for diffusion in the negative X direction):



$$N = D \frac{\partial C}{\partial X} = D \rho_m \frac{\partial Y}{\partial X} \text{ g-moles/cm}^2 \text{ sec} \qquad (1)$$

where: N = flux of SO_2 span gas (g-moles/cm^2 sec)
D = diffusion coefficient for SO_2 (cm^2/sec)
C = concentration of SO_2 (g-moles/cc)
Y = mole fraction of SO_2
ρ_m = molar density of gas (g-moles/cc)
X = linear distance (cm)

A material balance on a differential slice of calibration line gives:

$$\text{Input} = N|_{X+\Delta X}\, A\, \Delta t(\text{g-moles}) = D\, \rho_m\, A\, \Delta t(\partial Y/\partial X)|_{X+\Delta X}$$

$$\text{Output} = N|_{X+\Delta X}\, A\, \Delta t(\text{g-moles}) = D\, \rho_m\, A\, \Delta t(\partial Y/\partial X)|_{X}$$

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$$\text{Accumulation} = A\,\Delta X\,\rho_m\,Y|_{t+\Delta t} - A\,\Delta X\,\rho_m\,Y|_t \text{ (g-moles)}$$

where: A = cross-sectional area of calibration line (cm^2)
t = time from introduction of sample (sec)

These terms combine to give the equation:

$$\frac{\partial Y}{\partial t} = D\,\frac{\partial^2 Y}{\partial X^2} \tag{2}$$

The problem is simplified somewhat by using the dimensionless parameter $\theta = Y/Y_i$, where Y_i is the SO_2 mole fraction at $t = 0$ throughout the calibration line. With this substitution, Equation (2) becomes:

$$\frac{\partial \theta}{\partial t} = D\,\frac{\partial^2 \theta}{\partial X^2}$$

The boundary conditions are:

(1) At $t = 0$ $\quad \theta = 1 \quad$ for all $X > 0$
(2) At $X = 0$ $\quad \theta = 0 \quad$ for all $t > 0$
(3) At $X = \infty$ $\quad \theta = 1 \quad$ for all finite t

The above equation and boundary conditions have been previously solved by a number of authors (e.g., 27 and 28) in relation to unsteady-state heat transfer in an infinite slab. The solution for θ in terms of the error function is:

$$\theta = \text{erf}\left(\frac{X}{2\sqrt{Dt}}\right)$$

To determine the flux into the sample stream, the concentration gradient must be determined at $X = 0$:

$$\frac{\partial \theta}{\partial X} = \frac{1}{\sqrt{\pi D t}}\,\exp(-X^2/4Dt)$$

and

$$\left.\frac{\partial \theta}{\partial X}\right|_{X=0} = \frac{1}{\sqrt{\pi D t}}$$

By Equation (1):

$$\text{Flux into sample stream} = \frac{D\ \rho_m\ Y_i}{\sqrt{\pi D t}}\ \frac{\text{g-moles}}{\text{cm}^2\ \text{sec}}$$

To determine the response effect of this diffusive flux, a calculation will be made of the time required for the concentration of SO_2 in the sample to drop to 5% of the span gas concentration (95% response time). The following is assumed:

Sample flow rate = 1 slpm
Temperature = 0°C
Pressure = 101.3 N/m^2
$D = 0.104\ cm^2/sec$ for SO_2
Tube i.d. = 4.318 mm (6.35 o.d. x 1.016 wall)

A material balance on SO_2 around the mixing point gives:

Input due to flow = 0

$$\text{Input from calibration line} = \frac{D\ \rho_m\ Y_i\ A}{\sqrt{\pi D t}}\ \frac{\text{g-moles}}{\text{sec}}$$

$$\text{Output to analyzer} = \dot{m}\ Y$$

where: $\dot{m}$ = sample flow rate (g-moles/sec) = 7.436×10^{-4}

Equating input to output and solving for t gives:

$$t^{1/2} = \frac{D\ \rho_m\ A}{\dot{m}(\pi D)^{1/2}}\ \frac{Y_i}{Y}$$

For 95% response, $Y_i/Y = 20$.

$$t^{1/2} = \frac{(0.104)(4.461 \times 10^{-5})(0.1464)(20)}{(7.436 \times 10^{-4})(0.5716)}$$

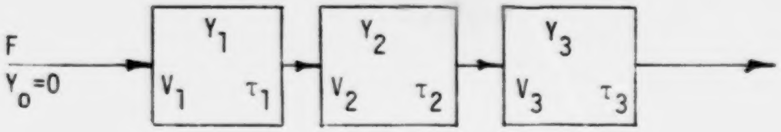
$$t = 1.02 \times 10^{-3} \text{ sec}$$

This calculation indicates that under all practical conditions, dead volumes have a negligible effect on response time.

APPENDIX E

RESPONSE CHARACTERISTICS OF BACK-MIXING VOLUMES

The various mixing volumes can be considered to be connected end to end with negligible transport time between consecutive volumes. Initially, the concentration is uniform at a mole fraction of Y_i. At time zero, a sample containing zero concentration flows into the first volume at a rate F. Perfect mixing is assumed in each volume.



The general equation relating mole fraction to time can be derived by considering volume 2.

$$\text{Input: } F\, Y_1\, \Delta t \text{ liters}$$

$$\text{Output: } F\, Y_2\, \Delta t \text{ liters}$$

$$\text{Accumulation: } V_2(Y_2|_{t+\Delta t} - Y_2|_t) \text{ liters}$$

where: F = volumetric flow rate (lpm)
Y_1 = mole fraction in and leaving volume 1
Y_2 = mole fraction in and leaving volume 2
V_2 = volume of volume 2 (liters)
t = time (min)

These terms lead to the following differential equation:

$$Y_2 - Y_1 = -\frac{V_2}{F}\frac{d\,Y_2}{dt}$$

The time constant for volume 2 is defined as:

$$\tau_2 \equiv \frac{V_2}{F} \tag{1}$$

and the differential equation becomes:

$$\frac{d\,Y_2}{dt} + \frac{Y_2}{\tau_2} = \frac{Y_1}{\tau_2} \tag{2}$$

This can be solved by introducing the integrating factor exp (t/τ_2):

$$\exp(t/\tau_2)\;dY_2 + \frac{Y_2}{\tau_2}\exp(t/\tau_2)\;dt = \frac{Y_1}{\tau_2}\exp(t/\tau_2)\;dt$$

The left-hand side is recognized as the derivative of $Y_2 \exp(t/\tau_2)$ so:

$$Y_2 \exp(t/\tau_2) = \frac{1}{\tau_2}\int Y_1 \exp(t/\tau_2)\;dt + C$$

or in general terms, where n is the volume number:

$$Y_n = \frac{\exp(-t/\tau_n)}{\tau_n}\int Y_{n-1}\exp(t/\tau_n)\;dt + C\exp(-t/\tau_n) \tag{3}$$

Except where $n = 1$, Y_{n-1} is a function of t and cannot be removed from the integral. The boundary condition for evaluation of the integration constant is:

At $\quad t = 0 \quad Y_n = Y_i \quad$ for all n

A. UNEQUAL TIME CONSTANTS

1. One Volume

For one volume, $n = 1$, $Y_{n-1} = Y_o = 0$, $C = Y_i$ and

$$\frac{Y_1}{Y_i} = \exp(-t/\tau_1) \tag{4}$$

2. Two Volumes

For two volumes in sequence, $n = 2$, $Y_{n-1} = Y_1$ given above and Equation (3) becomes:

$$Y_2 = \frac{\exp(-t/\tau_2)}{\tau_2} Y_i \int \exp\left[t\left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right)\right] dt + C \exp(-t/\tau_2)$$

after integration and rearrangement:

$$C = Y_i\left(1 - \frac{\tau_1}{\tau_1-\tau_2}\right)$$

and

$$\frac{Y_2}{Y_i} = \exp(-t/\tau_2) - \frac{\tau_1}{\tau_1-\tau_2} \left|\exp(-t/\tau_2) - \exp(-t/\tau_1)\right| \qquad (5)$$

3. Three Volumes

For three volumes, $n = 3$, and Y_{n-1} is given by Equation (5). Substituting in Equation (3), integrating, and rearranging gives:

$$C = 1 + \frac{\tau_1\tau_2}{(\tau_1-\tau_2)(\tau_2-\tau_3)} - \frac{\tau_1^{\ 2}}{(\tau_1-\tau_2)(\tau_1-\tau_3)} - \frac{\tau_2}{\tau_2-\tau_3}$$

and

$$\frac{Y_3}{Y_i} = \exp(-t/\tau_3) + \frac{\tau_2^{\ 2}}{(\tau_1-\tau_2)(\tau_2-\tau_3)} \left|\exp(-t/\tau_3) - \exp(-t/\tau_2)\right|$$

$$- \frac{\tau_1^{\ 2}}{(\tau_1-\tau_2)(\tau_1-\tau_3)} \left|\exp(-t/\tau_3) - \exp(-t/\tau_1)\right| \qquad (6)$$

Equations (4), (5), and (6) give, respectively, the output as a function of time from one, two, and three consecutive volumes.

B. EQUAL TIME CONSTANTS

For the special case in which the time constant is the same for each volume, a much simpler result is obtained.

1. One Volume

For one volume, the result is identical to Equation (4):

$$\frac{Y_1}{Y_i} = \exp(-t/\tau) \qquad (7)$$

2. Two Volumes

For two volumes, Equation (3) gives:

$$Y_2 = \frac{\exp(-t/\tau)}{\tau} Y_i \int dt + C \exp(-t/\tau)$$

which gives $C = Y_i$

and

$$\frac{Y_2}{Y_i} = \left(1 + \frac{t}{\tau}\right) \exp(-t/\tau) \qquad (8)$$

3. Three Volumes

For three volumes, the use of Equation (8) in Equation (3) gives $C = Y_i$ and

$$\frac{Y_3}{Y_i} = \left(1 + \frac{t}{\tau} + \frac{t^2}{2\tau^2}\right) \exp(-t/\tau) \qquad (9)$$

4. General Result

Continuation of the above procedure leads to the following general equation:

$$\frac{Y_N}{Y_i} = \left(1 + \sum_{n=1}^{N} \frac{t^n}{n!\ \tau^n}\right) \exp(-t/\tau) \qquad (10)$$

where N is the number of consecutive volumes with equal time constants.

C. SAMPLE CALCULATION OF SYSTEM RESPONSE TIME

To illustrate the above equations, the 95% response time will be calculated for the following hypothetical sampling system:

Plug-flow volume (sample lines and interconnecting tubing): 60.96 m of 6.35 o.d. x 1.016 mm tubing

Back-mixing volumes: pump = 200 cm^3
trap = 500 cm^3
analyzer cell = 400 cm^3

Sample flow rate = 1 lpm

First, the response time for the mixing volumes will be determined by Equation (6). The time constants are:

$$\tau_1 = 0.20 \text{ liters/1 lpm} = 0.20 \text{ min}$$

$$\tau_2 = 0.50 \text{ min}$$

$$\tau_3 = 0.40 \text{ min}$$

For 95% response, $Y_3/Y_i = 0.05$. The coefficients for Equation (6) are:

$$\frac{\tau_2^{\,2}}{(\tau_1-\tau_2)(\tau_2-\tau_3)} = -8.333$$

$$\frac{\tau_1^{\,2}}{(\tau_1-\tau_2)(\tau_1-\tau_3)} = 0.6667$$

Substituting into Equation (6) gives:

$$0.05 = \exp(-2.5t) - 8.333[\exp(-2.5t) - \exp(-2t)]$$

$$- 0.6667 [\exp(-2.5t) - \exp(-5t)]$$

This equation is solved by trial and error to give:

$$t = 2.39 \text{ min}$$

For the plug-flow volume, the total volume is:

$$V = \frac{(\pi)(0.17)^2(200)(12)(2.54)^3}{(4)(10^3)} = 0.893 \text{ liters}$$

The lag time for this volume is:

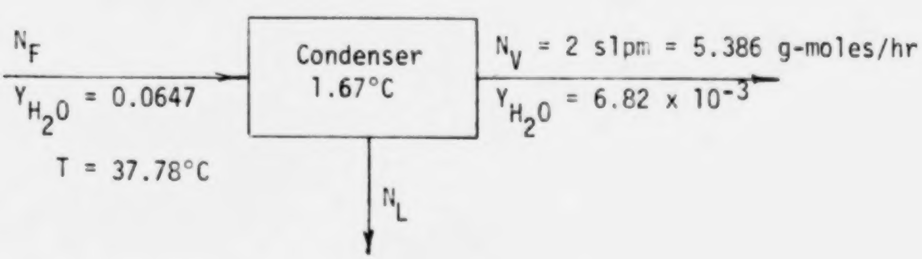
$$t = \frac{V}{F} = \frac{0.893 \text{ liters}}{1 \text{ lpm}} = 0.893 \text{ min}$$

The total 95% response time of the sampling system is 3.28 minutes. Of the total response time, 27% is due to plug flow and 73% due to back mixing.

APPENDIX F

CONDENSER COOLING REQUIREMENT

The feed is assumed to be saturated at 37.78°C. If the total moisture content is 15%, then a large fraction of the moisture entering the condenser is in the liquid phase. The cooling requirement for this liquid will be added onto the cooling requirement for the saturated gas stream determined below.



N_F
$Y_{H_2O} = 0.0647$
$T = 37.78°C$
Condenser
1.67°C
N_V = 2 slpm = 5.386 g-moles/hr
$Y_{H_2O} = 6.82 \times 10^{-3}$
N_L

Water balance on condenser:

$$0.0647\ N_F = 6.82 \times 10^{-3}\ N_V + N_L$$

$$N_F = N_V + N_L$$

Substituting N_V and solving simultaneously gives:

$$N_F = 5.719 \text{ g-moles/hr} = 0.165 \text{ kg/hr}$$

$$N_L = 0.333 \text{ g-moles/hr} = 5.99 \times 10^{-3} \text{ kg/hr}$$

$$N_V = 5.386 \text{ g-moles/hr} = 0.155 \text{ kg/hr}$$

Heat capacity for air = 1.495 kjoules/kg-°C
Heat capacity for water = 4.186 kjoules/kg-°C
Latent heat of vaporization = 2511.4 kjoules/kg

$$\text{Air: } q_a = W\ C_p\ \Delta T = (0.155 \frac{\text{kg}}{\text{hr}}) (\frac{1.495 \text{ kjoules}}{\text{kg-°C}}) (36.11°C) = 8.367 \text{ kjoules/hr}$$

Condensation: $q = W\,\lambda = (5.99 \times 10^{-3}\ \frac{kg}{hr})\ (\frac{2511.4\ kjoule}{kg}) = 15.04\ \frac{kjoule}{hr}$

Liquid water: $q = W\,C_p\,\Delta T = (5.99 \times 10^{-3}\ \frac{kg}{hr})(4.186\ \frac{kjoule}{kg - {}^\circ C})\ (\sim 17.78^\circ C) = .446\ \frac{kjoule}{hr}$

Total cooling requirement = 23.8 kjoule/hr

If the feed contains 16% moisture:

$$(0.0647)(5.719) + (1.0)\ N_{FL} = 0.16(5.719 + N_{FL})$$

where N_{FL} is the moles per hour of liquid condensate fed to the condenser.

$$N_{FL} = 0.649 \text{ g-moles/hr} = 0.0116 \text{ kg/hr}$$

The cooling requirement for this liquid flow is:

$$q = W\,C_p\,\Delta T = (0.0116\ \frac{kg}{hr})\ (4.186\ \frac{kjoule}{kg - {}^\circ C})\ (36.11^\circ C) = 1.76\ \frac{kjoules}{hr}$$

The total cooling requirement is about 25.56 kjoules/hr.
The total condensate to be removed is about 18 ml/hr.

APPENDIX G

SPECIFICATIONS FOR SAMPLING INTERFACE

The specifications for a sampling interface following the flow diagram of Figure I-1 are given below.

A. SAMPLE PROBE/COARSE FILTER

Probe tip to be 316 SS tubing 6.35 mm o.d. open to downstream direction. Probe tip to be connected via 316 SS compression fittings to 316 SS check valve. Cracking spring pressure in check valve to be as small as possible (less than 3.45 N/m^2 preferred). Coarse particulate filter to be alundum thimble in stainless steel housing. Provisions must be made for admitting calibration gas upstream of the coarse filter. Calibration gases to be admitted via 6.35 o.d. 316 SS tube and compression fitting tee. Entire sampling probe assembly (including probe tip, check valve, calibration tee, and alundum filter) to be mounted inside stack with feedthroughs provided for calibration gas inlet and sample outlet. All materials in contact with sample or calibration gas to be 316 SS, teflon or viton.

Fabricate from following materials:

Probe tip - 6.35 mm o.d. 316 SS x 0.889 mm wall tube

Connection to check valve - 6.35 mm tube x 6.35 mm pipe female connector compression fitting - 316 SS

Check valve - 6.35 mm NPT male connections. Lowest possible spring pressure. 316 SS. Viton seat.

Calibration tee - 6.35 mm NPT Tee, 316 SS

Connection to calibration line - 6.35 mm tube x 6.35 mm pipe male angle connector. Compression fitting - 316 SS

Calibration line - 6.35 mm o.d. - 316 SS x 0.762 mm wall tube

Connection to filter - 6.35 mm close nipple 6.35 mm x 12.7 mm red. bush. Both in 316 SS.

Filter - alundum particulate sampling thimble; SS holder with 12.75 mm NPT female ports

Sampling line connection - 6.35 mm x 12.75 mm NPT red. bush, 6.35 mm tube x 6.35 NPT male connector compression fitting,both 316 SS.

Probe assembly to be inserted through 7.62 cm pipe stack sampling port with lines exiting through 7.62 cm NPT cap (or plug).

B. SAMPLE LINES

Outdoor service where freezing is possible, on moisture-containing stacks: Dekoron electrically traced teflon 6.35 mm o.d. tube x 0.762 mm wall. Variac to be used as power supply and power adjusted to prevent temperature drop below freezing point. Outdoor service on dry stacks and indoor service on all stacks. 6.35 o.d. x 1.016 mm wall polypropylene tubing. Maximum temperature for pp = 107.2°C.

C. CALIBRATION GAS LINES

Calibration gases to be dry. Use unheated polypropylene with nylon compression fittings. 6.35 mm o.d. x 1.016 mm wall.

D. VENT LINES

Use 6.35 mm o.d. polyethylene x 1.016 mm wall. If line extends more than several inches outside, use heat traced Teflon to prevent constriction due to freezing where subfreezing temperatures are possible.

E. SAMPLING PUMP

Sampling pump to be a diaphragm type. Internal parts to be Teflon Required flow = 2 slpm (4.24 scfh) into 20.68 k N/m^2 with suction at -13.79 k N/m^2 (4" Hg Vac). Buy Thomas Industries 107CA110.

Pump must be piped with discharge-to-suction bypass. Make loop volume small as practically possible. Use Whitey needle valve with 6.35 mm Swagelok tube connections. Maximum flow = 14.16 sl/min. Take maximum ΔP = 6.895 k N/m^2 $\therefore$ min. C_v factor = 0.130. Buy Whitey 1RS4-316 with 4.369 mm orifice. Also use two nylon tees, 6.35 mm tube, Swagelok.

F. PRESSURE GAUGES

Both gauges to be 316 SS tip and tube. Standard accuracy (± 2%) PI-1 -34.47 to +34.47 kN/m^2, PI-2 0-68.95 kN/m^2. Prefer 6.35 mm NPT lower male connection.

G. LIQUID TRAP

To be a ball float trap of stainless steel construction. Liquid removal required: 20 ml/hour. Buy Armstrong 11-LD. Constructed of 304 and 440 stainless steel. Top port 3/4 NPT female. Bottom port 1/2 NPT female.

Top connections:

19.05 x 6.35 NPT red. bush - 316
6.35 NPT x close nipple - 316
6.35 NPT tee - 316
2 - 6.35 tube x 6.35 NPT male connectors - one bored through nylon

Bottom connections:

12.7 x 6.35 NPT red. bush - 316
6.35 tube x 6.35 NPT male connector - nylon

H. FLOW METERS

Nominal flow for all instruments = 1 slpm = 2 scfh. Flow meter to include integral SS metering valve. Buy Dwyer RMS-3-SSV.

I. FINE FILTER

Fabricate from glass wool in a glass tube. Use approximately 12.7 mm diameter glass tube. Pack with glass wool until a "reasonable" flow resistance is obtained. Butt-connect to system with tygon tubing.

J. REFRIGERATED CONDENSER

To be of 316 SS construction. Cooling requirement very small = 23 kjoules/hr. Buy smallest unit available. Buy Hankison E-3GSS with three cooling coils for contingencies.

K. AUTOMATIC CALIBRATION SYSTEM

Automatic calibration to occur every 24 hours ± 15 minutes. Each of three calibration gases is to be admitted to analyzer in turn for a period of 10 minutes each. System schematic shown in Figure I-10.

Parts List

(1) Zenith Model 2400-1 24-hour timer.

(2) Eagle Model 340 #MP-4-A6-22 with cycle gear MP5-44 and #HN320 enclosure. 33-minute timer.

(3) Three toggle switches DPST - contacts rated at 1 amp.

(4) Three pilot lights 115 VAC. High impedance neon.

(5) Two conductor cables needed. 18 gauge 300 volt. Insulation suitable for outdoors.

(6) Solenoids - stainless steel

  (a) 2-way #8262C7 ASCO

  (b) 3-way #832061 ASCO

(7) 1/4" compression fittings

  8 - 1/4" tube x 1/4 NPT male connectors - nylon

  1 - 1/4" tube union - 316

  1 - 1/4" tube x 1/4 NPT male connector - 316

(8) Pipe fittings 316 SS

  1 - 1/4 NPT cross

  3 - 1/4 NPT x close nipple

APPENDIX H
SOURCES OF SAMPLING SYSTEM COMPONENTS

A. PROBE-TIP FILTERS

1. ASCO Sintering Co.
   3000 S. Vail Ave.
   Los Angeles, Calif.

2. Leeds & Northrup Co.
   North Wales, Pa. 19454

3. Mott Metallurgical Corp.
   Spring Lane
   Farmington Industrial Park
   Farmington, Conn. 06032

4. Pall Trinity Micro Corp.
   Cortland, N. Y. 13045

INTERNAL TYPE (ALUNDUM THIMBLES)

1. American Hospital Supply Corp.
   Scientific Products Division
   1210 Leon Place
   Evanston, Illinois 60201

2. Balston, Inc.
   703 Mass. Ave.
   Lexington, Mass. 02173

3. Research-Cottrell, Inc.
   P. O. Box 750
   Bound Brook, N. J. 08805

4. Van Waters & Rogers, Inc.
   P. O. Box 3200
   Rincon Annex
   San Francisco, Calif. 94119

5. Western Precipitation Co.
   1000 W. Ninth Street
   Los Angeles, California 90015

INTERNAL TYPE (OTHER)

1. BGI Inc.
   1254 Main Street
   Waltham, Mass. 02154

2. Flotronics Div. of Selas Corp.
   Spring House, Pa. 19477

3. Gelman Instrument Co.
   600 Wagner Rd.
   Ann Arbor, Mich. 48106

B. FINE FILTERS

1. Balston, Inc.
   P. O. Box C
   703 Mass. Ave.
   Lexington, Mass. 02173

2. Creative Scientific Equipment Corp.
   2305 Cherry Industrial Circle
   Long Beach, Calif. 90805

3. Flotronics Div. of Selas Corp.
   Spring House, Pa. 19477

4. Gelman Instrument Co.
   600 S. Wagner Rd.
   Ann Arbor, Mich. 48106

5. Millipore Corp.
   Bedford, Mass. 01730

6. Mine Safety Appliance Co.
   201 N. Braddock Ave.
   Pittsburgh, Pa. 15208

7. Pall Trinity Micro Corp.
   Cortland, N. Y. 13045

C. REFRIGERATION UNITS

1. Cole-Parmer
   7425 N. Oak Park Ave.
   Chicago, Ill. 60648

2. FTS Systems, Inc.
   P. O. Box 158
   Stone Ridge, N. Y. 12484

3. Hankinson Corp.
   Cannonsburg, Pa. 15317

4. Markson Science, Inc.
   P. O. Box 767
   Del Mar, Calif. 92014

5. Neslab Instruments, Inc.
   871 Islington St.
   Portsmouth, N. H. 03801

6. Tecumsch Products Co.
   Refrigeration Division
   Tecumsch, Mich. 49286

D. PERMEATION DRYERS

1. Perma Pure Products, Inc.
P. O. Box 70
Oceanport, N. J. 07757

E. SAMPLE PUMPS

1. (Aspirator type)
Air-Vac Engineering Co., Inc.
100 Gulf St.
Milford, Conn. 06460

2. Gelber Pumps
5806 N. Lincoln Ave.
Chicago, Ill. 60659

3. Metal Bellows Corp.
1075 Providence Hwy.
Sharon, Mass. 02067

4. Thomas Industries
1419 Illinois Ave.
Sheboygan, Wis. 53081

F. HEAT-TRACED SAMPLE LINES

1. Samuel Moore & Co.
Dekoron Division
Industrial Park
Mantua, Ohio 44255

G. LIQUID CONDENSATE TRAPS

1. Armstrong Machine Works
Three Rivers, Mich. 49093

2. Nicholson Div. of Electronic Specialty Co.
12 Oregon St.
Wilkes-Barre, Pa. 18702

3. Sarco Co., Inc.
1951 26th St., S.W.
Allentown, Pa. 18105

H. PRESSURE GAUGES AND MANOMETERS

1. Alnor Instrument Co.
420 N. LaSalle St.
Chicago, Ill. 60610

2. F. W. Dwyer Mfg. Co.
   P. O. Box 373
   Michigan City, Ind. 46360

3. Meriam Instrument Co.
   10920 Madison Ave.
   Cleveland, Ohio 44102

4. Research-Cottrell, Inc.
   P. O. Box 750
   Bound Brook, N. J. 08805

5. Western Precipitation Co.
   1000 W. Ninth St.
   Los Angeles, Calif. 90015

I. NEEDLE VALVES

1. American Instrument Co.
   8030 Georgia Ave.
   Silver Spring, Md. 20901

2. Cajon Co.
   32550 Old South Miles Rd.
   Salon, Ohio 44139

3. Hoke Manufacturing Co.
   P. O. Box 501
   Tenafly, N. J. 07670

4. Nupro Company
   15635 Saranac Rd.
   Cleveland, Ohio 44110

5. Whitey Research Tool Co.
   5679 Landregan St.
   Emeryville, Calif. 94608

J. ROTAMETERS

1. Brooks Instrument Co.
   407 W. Vine St.
   Hatfield, Pa. 19440

2. F. W. Dwyer Mfg. Co.
   P. O. Box 373
   Michigan City, Ind. 46360

3. Fischer & Porter, Inc.
   County Line Rd.
   Warminster, Pa. 18974

4. Ideal Precision Glass Co.
   Manostat Division
   P. O. Box 287
   Carlstadt, N. J. 07072

5. Meriam Instrument Co.
   10920 Madison Ave.
   Cleveland, Ohio 44102

6. Schutte & Koerting, Inc.
   2239 State Rd.
   Cornwells Heights
   Bucks County, Pa. 19020

K. TUBING FITTINGS

1. Cajon Co.
   32550 Old South Miles Rd.
   Solon, Ohio 44139

2. Crawford Fittings Co.
   29500 Solon Rd.
   Solon, Ohio 44139

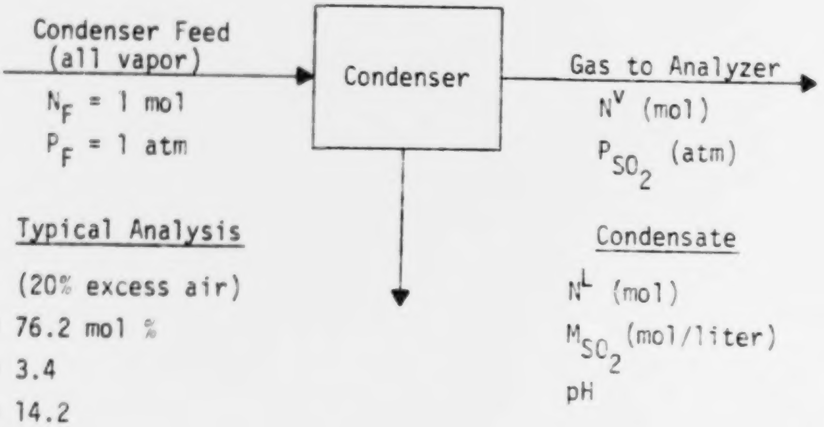
3. D & G Plastics Co.
   P. O. Box 209
   Kent, Ohio 44240

4. Hoke Manufacturing Co.
   P. O. Box 501
   Tenafly, N. J. 07670

APPENDIX I

CALCULATION OF SO_2 LOSS AND pH OF CONDENSATE

The following calculation (33) gives condenser losses and pH of the condensate for various gas phase concentrations of SO_2. A constant water content of 6% is assumed.


Condenser Feed
(all vapor)
N_F = 1 mol
P_F = 1 atm
Condenser
Gas to Analyzer
N^V (mol)
P_{SO_2} (atm)
Condensate
N^L (mol)
M_{SO_2} (mol/liter)
pH

Typical Analysis

(20% excess air)

N_2 = 76.2 mol %
O_2 = 3.4
CO_2 = 14.2
H_2O = 6.0
SO_2 = 0.2 (from 3%S in coal)
SO_3 = trace

Given: $P_{SO_2,F}$ = partial pressure (atm) of SO_2 in feed
$P_{W,F}$ = partial pressure (atm) of water in feed
T_c = condenser temperature

Determine: P_{SO_2} = partial pressure (atm) of SO_2 in off-gas
M_{SO_2} = total dissolved SO_2 in condensate
pH = pH of condensate

(Note: M_{SO_2} is a unique function of pH of condensate. Therefore, pH can potentially be used to correct gas analysis for SO_2 loss in condensate.)

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Worst Case: (1) Assume all water is condensed.

(2) Assume condensate and off-gas reach equilibrium with respect to dissolved SO_2.

A. SO_2-H_2O VAPOR-LIQUID EQUILIBRIUM

T = °K

$$SO_2(v) = SO_2(aq) \qquad K_4 = \frac{[SO_2(aq)]}{P_{SO_2}} \frac{\left(\frac{mol}{\ell}\right)}{(mm\ Hg)} \qquad \log_{10}K_4 = \frac{1368.43}{T} - 7.3756 \qquad (1)$$

$$SO_2(aq) + H_2O = H^+ + HSO_3^- \qquad K_{1A} = \frac{[H^+][HSO_3^-]}{[SO_2(aq)]} \qquad \log_{10}K_{1A} = \frac{843.33}{T} - 4.7150 \qquad (2)$$

$$HSO_3^- = H^+ + SO_3^= \qquad K_{2A} = \frac{[H^+][SO_3^=]}{[HSO_3^-]} \qquad \log_{10}K_{2A} = -7.2 (@\ 25°C) \qquad (3)$$

(results not sensitive to K_{2A})

$$H_2O = H^+ + OH^- \qquad K_W = [H^+][OH^-] \qquad \log_{10}K_W = -14 (@\ 25°C) \qquad (4)$$

(results not sensitive to K_W)

$$[SO_2] = \text{total dissolved } SO_2 = [SO_2(aq)] + [HSO_3^-] + [SO_3^=]$$

Unknowns: $[H^+]$, $[OH^-]$, $[SO_2(aq)]$, $[HSO_3^-]$, $[SO_3^=]$ = 5

Use four equations above plus:

$$\text{Electrical Neutrality:} \quad [H^+] = [HSO_3^-] + 2[SO_3^=] + [OH^-] \qquad (5)$$

Method of Solution: Solve for one of the sensitive variables as a function of P_{SO_2}. Insensitive variables (species present in minor amounts) are OH^-, $SO_3^=$. Eliminate these from Equation (5) using Equations (4) and (3), (5) becomes:

$$[H^+] = [HSO_3^-] + \frac{2K_2[HSO_3^-]}{[H^+]} + \frac{K_W}{[H^+]} \qquad (6)$$

Use Equations (1) and (2) in (6) to eliminate $[HSO_3^-]$ and $[SO_2(aq)]$, thereby obtaining $[H^+] = f(P_{SO_2})$.

$$[H^+] = [HSO_3^-] \quad 1 + \frac{2K_2}{[H^+]} + \frac{K_W}{[H^+]}$$

$$= \frac{K_1[SO_2(aq)]}{[H^+]} \quad 1 + \frac{2K_2}{[H^+]} + \frac{K_W}{[H^+]}$$

$$= \frac{K_1 K_H \; P_{SO_2}}{[H^+]} \quad 1 + \frac{2K_2}{[H^+]} + \frac{K_W}{[H^+]}$$

or

$$[H^+]^2 = K_1 K_H \; P_{SO_2} \quad 1 + \frac{2K_2}{[H^+]} + \frac{K_W}{[H^+]} \qquad (7)$$

Results of solving Equation (7) shown in Figure I-21.

Using $[H^+]$ found from solving Equation (7):

Calc $[SO(aq)]$ from Equation (1)
$[HSO_3^-]$ from Equation (2)
$[SO_3^=]$ from Equation (3)

then $[SO_2] = [SO_2(aq)] + [HSO_3^-] + [SO_3^=]$

Results shown in Figure I-22 ($[SO_2]$ vs pH). These are consistent with tabular data for SO_2 in water given in Perry's Handbook.

Therefore, calculational procedure was incorporated as a subroutine in subsequent calculations.

B. MATERIAL BALANCE AROUND CONDENSER

$$P_{SO_2,F}(\text{atm}) = P_{SO_2}(\text{atm}) \; N^V(\text{mol}) + [SO_2] \left(\frac{\text{mol}}{\ell}\right) \times \frac{N^L(\text{mol } H_2O)}{55\left(\frac{\text{mol } H_2O}{\ell}\right)}$$

Figure I-21. Partial Pressure SO_2 vs pH.

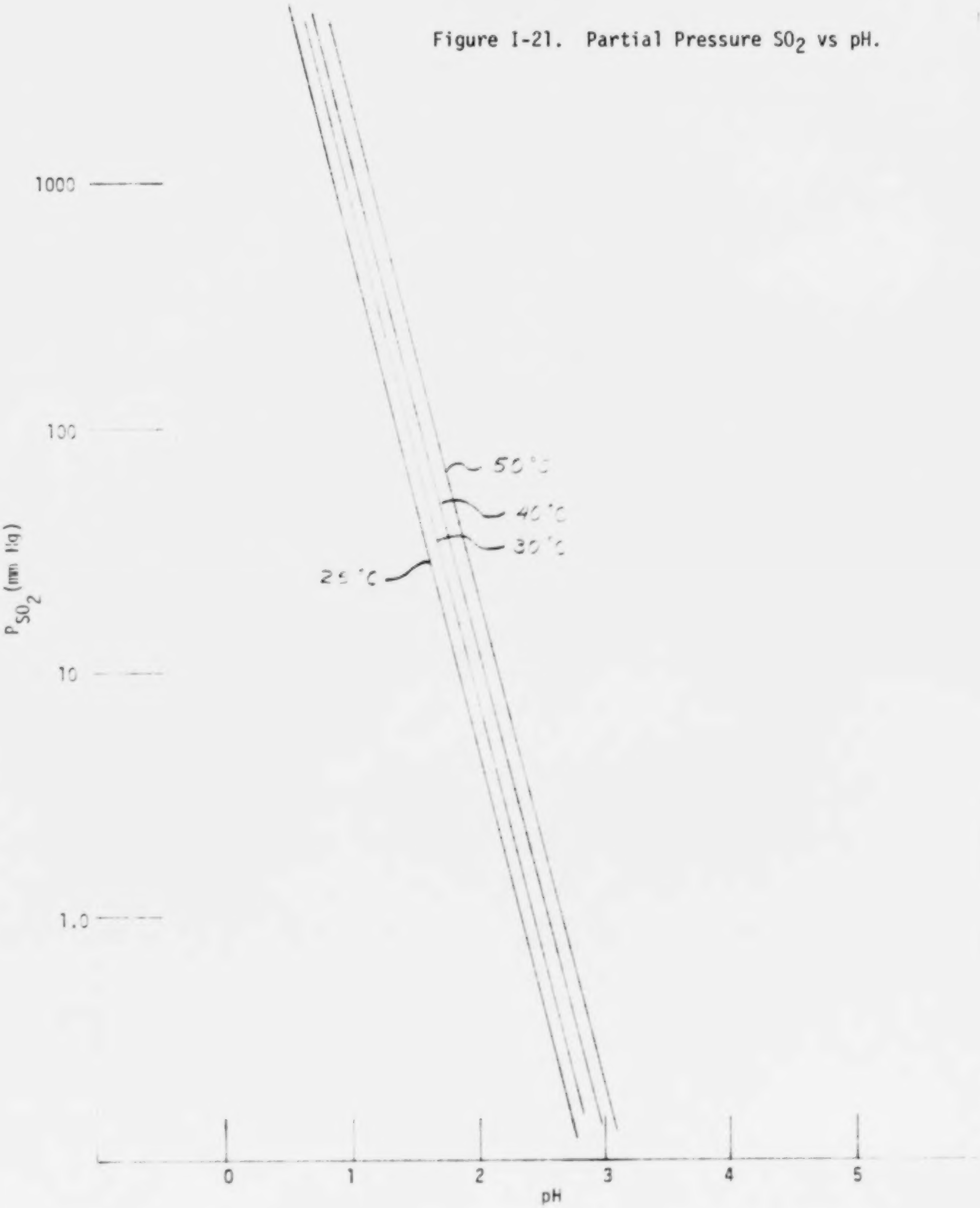
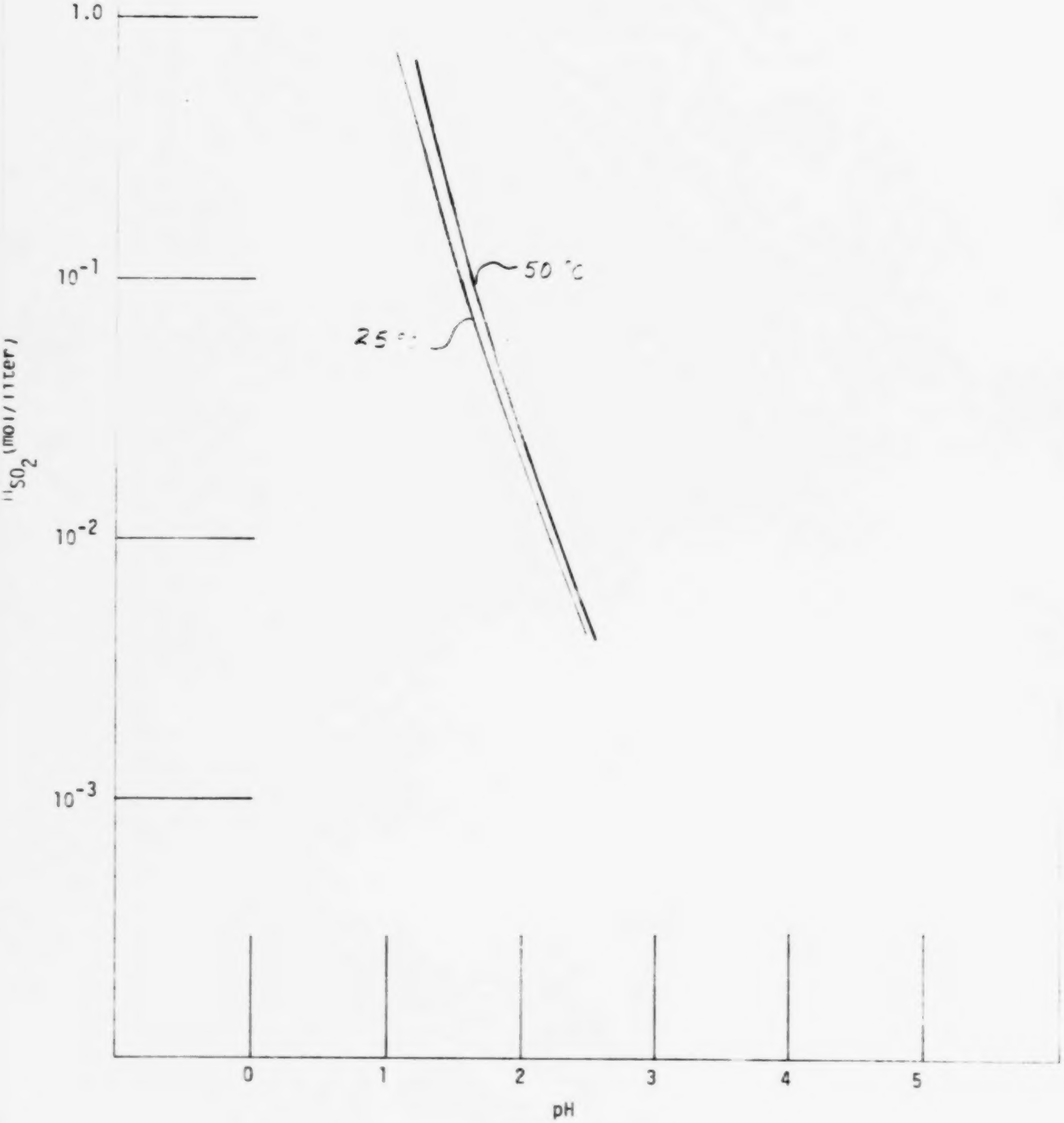


Figure I-22. Liquid Concentration of SO_2 vs pH.



$$P_{SO_2}(\text{atm}) = P_{SO_2,F}(\text{atm}) - \frac{[SO_2]N^L}{55} \;/N^V$$

$$P_{SO_2}(\text{mm Hg}) = \frac{760}{N^V} \;\; \frac{P_{SO_2,F}(\text{mm Hg})}{760} - \frac{[SO_2]N^L}{55}$$

$$P_{SO_2}(\text{mm Hg}) = \frac{1}{N^V} \;\; P_{SO_2,F}(\text{mm Hg}) - \frac{760}{55}\,[SO_2]N^L$$

Equation (8) is solved simultaneously with vapor-liquid equilibrium in attached Fortran program.

Fortran program, which can be used for any dibasic acid, is attached. Requires data of first and second ionization constants and Henry's Law constants (as f(T) if available).

Runs for SO_2 were made from $P_{SO_2,F}$ of 10^{-6} to 10^{-2} atm (1 to 10,000 ppm) at 25°C and 50°C, assuming 6% H_2O in feed and all water condenses.

Results indicate negligible loss of SO_2 in condensate.

NOTE: SO_2 is more soluble than nitric oxide and carbon dioxide. Therefore, these should not be effected by condenser. However, NO_2 is more soluble, but dissolution more complex.

$$(2NO_2 + H_2O = HNO_2 + H^+ + NO_3^-)$$

$$[3HNO_2 = H^+ + NO_3^- + 2NO + H_2O \text{ (slow in cold)}]$$

SO_2 CONDENSER LOSS

T(°C)	$P_{SO_2,F}$(atm)	N^V	N^L	$[SO_2]\ \frac{mol}{\ell}$	pH	P_{SO_2}(atm)	$\frac{P_{SO_2}}{P_{SO_2,F}}$
25.0	0.999E-06	0.940E 00	0.600E-01	0.122E-03	0.391E 01	0.920E-06	0.920E 00
25.0	0.199E-05	0.940E 00	0.600E-01	0.178E-03	0.375E 01	0.192E-05	0.960E 00
25.0	0.300E-05	0.940E 00	0.600E-01	0.221E-03	0.366E 01	0.293E-05	0.978E 00
25.0	0.399E-05	0.940E 00	0.600E-01	0.257E-03	0.359E 01	0.395E-05	0.989E 00
25.0	0.499E-05	0.940E 00	0.600E-01	0.289E-03	0.354E 01	0.498E-05	0.996E 00
25.0	0.600E-05	0.940E 00	0.600E-01	0.318E-03	0.350E 01	0.601E-05	0.100E 01
25.0	0.700E-05	0.940E 00	0.600E-01	0.345E-03	0.347E 01	0.704E-05	0.100E 01
25.0	0.799E-05	0.940E 00	0.600E-01	0.371E-03	0.344E 01	0.808E-05	0.101E 01
25.0	0.900E-05	0.940E 00	0.600E-01	0.394E-03	0.341E 01	0.912E-05	0.101E 01
25.0	0.999E-05	0.940E 00	0.600E-01	0.417E-03	0.339E 01	0.101E-04	0.101E 01

APPENDIX J

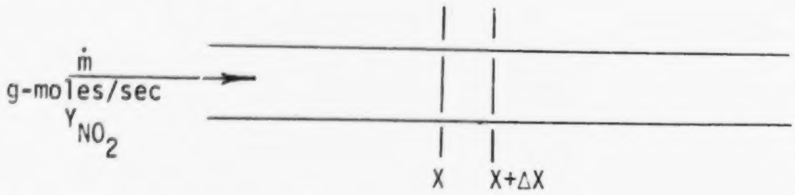
CALCULATION OF NO_2 ABSORPTION RATE

The rate of absorption of NO_2 from the sample stream can be calculated if the rate of mass transfer is known. It is assumed that the absorption is kinetically controlled with flux (35):

$$N = 25 \times 10^{-6}\, P_{NO_2}$$

where: N = flux in g-moles/cm^2 sec
P_{NO_2} = partial pressure NO_2 in atm

In the diagram below, the interior walls are assumed to be totally wetted with condensate.



A material balance on the differential element gives:

$$\text{Input} = \dot{m}\, Y_{NO_2}\big|_X$$

$$\text{Output} = \dot{m}\, Y_{NO_2}\big|_{X+\Delta X} + N\,\pi\,D\,\Delta X$$

$$\text{Accumulation} = 0$$

These terms combine to give:

$$-\frac{dP_{NO_2}}{dX} = 25 \times 10^{-6}\,\frac{\pi\, D\, P\, P_{NO_2}}{\dot{m}}$$

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where: P = total pressure (atm)
D = tube inside diameter (cm)
$\dot{m}$ = flow rate (g-moles/sec)
Y = mole fraction

This equation integrates to:

$$\ln \frac{(P_{NO_2})_{final}}{(P_{NO_2})_{initial}} = - 25 \times 10^{-6} \frac{\pi D P}{\dot{m}} X$$

For a flow rate of 2 slpm through a tube of 1/4 o.d. x 0.040 wall, the NO_2 concentration decreases by 50% in a tubing length of about 1 ft:

$$X = \frac{(1.487 \times 10^{-3})}{(25 \times 10^{-6})(\pi)(0.4318)(1)} \ln 0.50$$

$$X = 30.4 \text{ cm}$$

INVESTIGATION

OF

EXTRACTIVE SAMPLING INTERFACE PARAMETERS

PART II

FIELD DEMONSTRATION

INTRODUCTION

The third phase of this program was a field demonstration of interface systems designed according to the data and information presented in Part One of this report. Initially it was intended to demonstrate systems on the following Category I sources:

a. coal-fired power plant
b. oil-fired power plant
c. sulfuric acid power plant
d. nitric acid power plant

Due to lack of program resources only the two power plant systems were implemented.

In keeping with the principles described in Part One, the systems implemented were designed to demonstrate adequate interface systems in a minimum sense. Particularly, it was intended to demonstrate that probe filter backflushing is not necessary, that sample lines heated above the sample dewpoint are not necessary and that expensive samples line materials are not required. Also, it was intended to demonstrate a through-the-probe-tip-filter calibration system.

The results of the demonstration program are inconclusive. However, there is no evidence which would indicate that the assumptions underlying the major items mentioned above are in error. The inconclusive results stem from the difficulties of operating complex field programs with experimental equipment under difficult-to-impossible operating conditions. The latter included extremely inclement winter weather and frequent boiler shut-downs resulting from the energy crisis of the winter of 1973-1974.

Lessons from the experience of this field program included under-estimating the difficulties involved in the start-up of a newly designed system and the problems associated with the simultaneous demonstration of two systems using time-shared field crews.

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DESCRIPTION OF DEMONSTRATION SYSTEM

BACKGROUND

The measurement systems were designed according to the design information presented in our Interim Report. At the time of writing the Interim Report two general arrangements for pump and moisture removal systems were identified. These systems are depicted in Figure II-1. The system depicted in Figure II-1a was selected because removing condensate from a pressurized water knockout trap is considerably less difficult than from an evacuated trap. Furthermore, with the condensation taking place at the high pressure side of the pump, it is not subject to additional condensation forming before reaching the analyzers, whereas, this condition is to be expected for the case shown in Figure II-1b if the sample temperature conditions are about equal before the pump and before the analyzer.

The pump configuration chosen lead to problems with pump life which were not entirely unanticipated; however, the circumstances of seeking a minimum system favored the simpler instrumental trade-off for the potentially lower reliability of the pump.

All data collected were with a system of the type shown in Figure II-1a. However just before the end of the field program, an attempt was made to convert a system to one of the type shown in Figure II-1b, but no program resources remained for operation of the system. The detailed description of the fabrication requirements for the demonstration system is presented in Part One, Appendix G.

SAMPLING AND INSTRUMENTAL LOCATIONS

The demonstration program took place at two sites:

1. Boston Edison's Edgar Station at Weymouth, Massachusetts (Oil-fired plant)
2. Public Service Company of New Hampshire's Merrimack Station at Bow, New Hampshire (Coal-fired plant)

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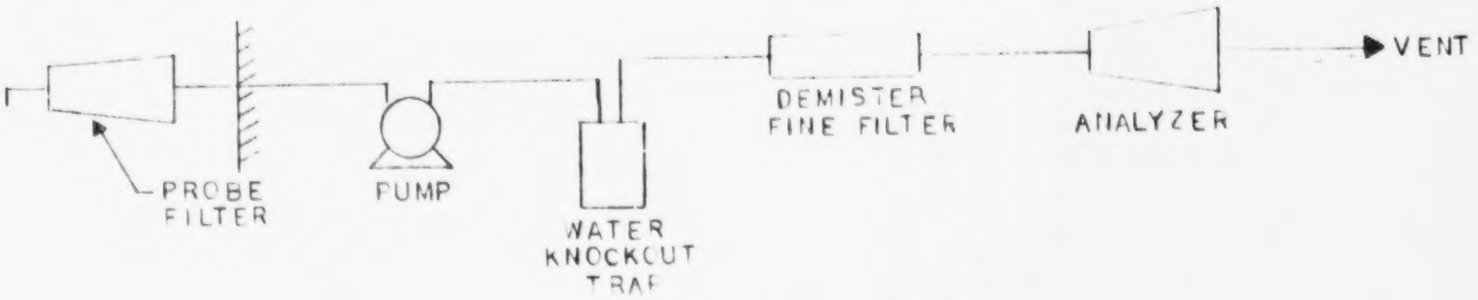

PROBE
FILTER
PUMP
WATER
KNOCKOUT
TRAP
DEMISTER
FINE FILTER
ANALYZER
VENT

Figure II-1a

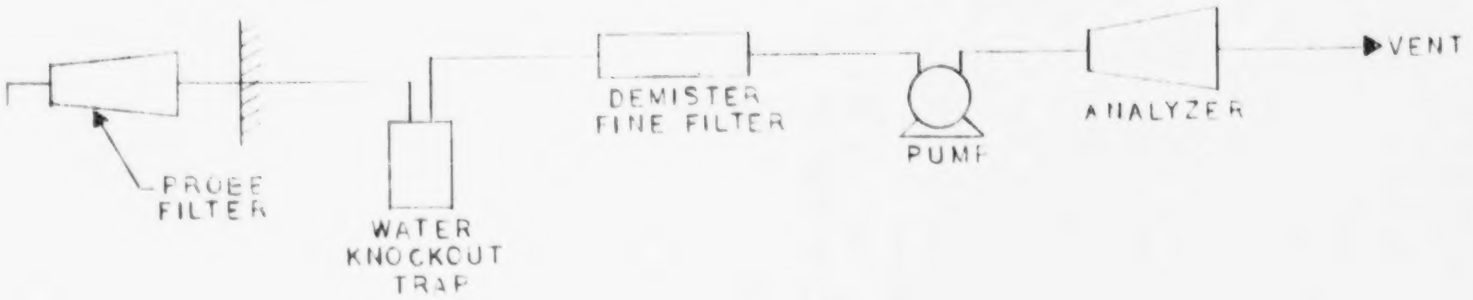

PROBE
FILTER
WATER
KNOCKOUT
TRAP
DEMISTER
FINE FILTER
PUMP
ANALYZER
VENT

Figure II-1b

Figure II-1. General Arrangement of Pump in Sampling Systems.

These plants were of different designs. The oil-fired plant was the stack through the roof design while the coal-fired plant was an inline design with the stack located outdoors behind the boiler. These power plant differences affected the sampling interface design only in the amounts of sampling line located outdoors and indoors. This line length was significant because electrically heated sampling lines were required and used for all outdoor exposures since the ambient temperatures during the demonstration periods were normally sub-freezing. Where exposed to the weather, sampling lines were insulated with electrically-traced Teflon (Dekoron TM). Sampling lines used indoors were simply polyproplene tubing.

The sampling line temperatures were not maintained above the sample dew point. Therefore, it was necessary to pitch the lines from the sampling probe back to the condensate knockout trap in order to drain condensate from the sampling lines.

Figures II-2 and II-3 depict the power plant configuration and interface installations for the oil-fired and coal-fired sites respectively.

FABRICATION OF SAMPLING SYSTEM

Probe Assembly

The probe assemblies were identical for both demonstration sites;only the depth of probe insertion varied. Insertion depths were 0.92 m and 0.76 m for the oil-fired and coal-fired sites respectively. The probe assembly incorporated the following features:

a. sample nozzle
b. coarse particulate filters
c. introduction point for zero and span gases
d. mechanical support for the above

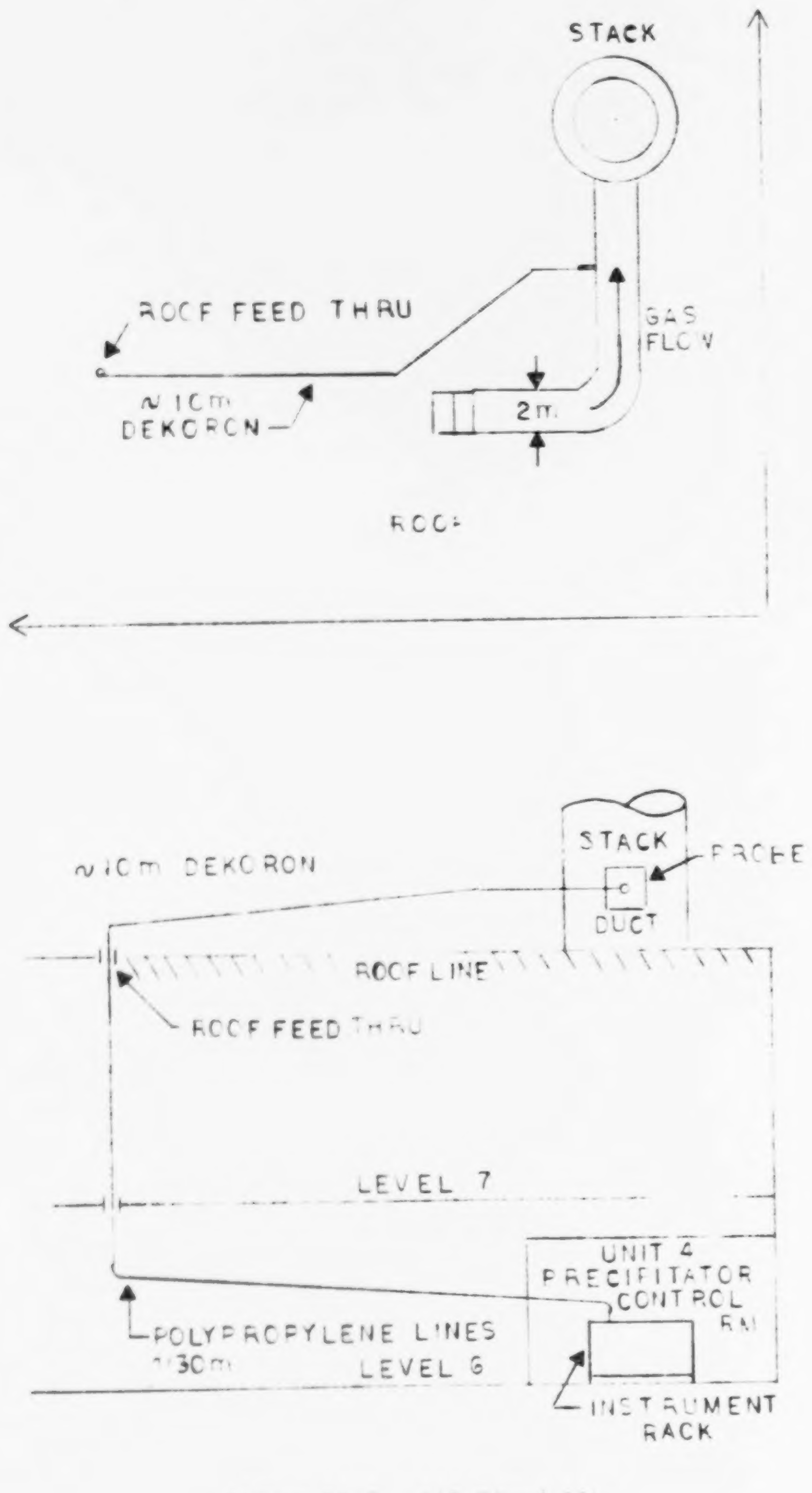
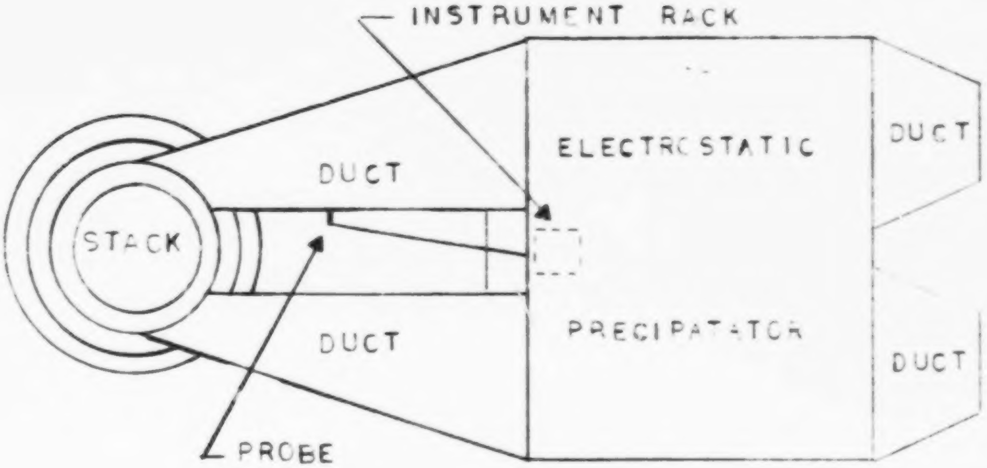
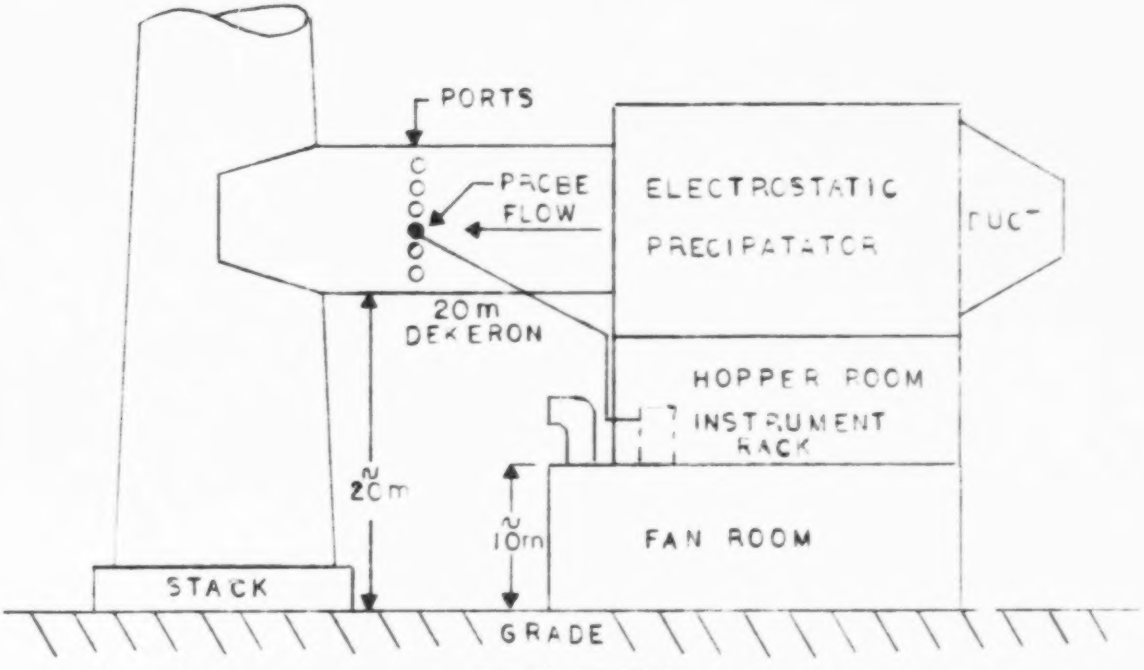

STACK
ROOF FEED THRU
GAS FLOW
2m
~10m DEKORON
ROOF
~10m DEKORON
STACK
PROBE
DUCT
ROOF LINE
ROOF FEED THRU
LEVEL 7
UNIT 4 PRECIPITATOR CONTROL RM
POLYPROPYLENE LINES ~30m
LEVEL 6
INSTRUMENT RACK

Figure II-2. Oil-Fired Site.


INSTRUMENT RACK
ELECTROSTATIC
PRECIPATATOR
DUCT
DUCT
DUCT
DUCT
STACK
PROBE

PLAN VIEW


PORTS
PROBE
FLOW
ELECTROSTATIC
PRECIPATATOR
DUCT
20m
DEKERON
HOPPER ROOM
INSTRUMENT
RACK
≈ 20m
≈ 10m
FAN ROOM
STACK
GRADE

ELEVATION

Figure II-3. Coal-Fired Site.

The arrangement of components is depicted in Figure II-4. During sampling, sample gas is drawn in through the downstream-facing nozzle, passes through the check valve in the forward direction and is filtered by a medium porosity (~5μm) alundum thimble. The filtered sample gas is then sucked through a 6.35 mm 316 stainless steel tube (located inside the black iron pipe support) to outside the duct wall; where a connection is made with the sampling line.

Sample gas is brought into the duct through a 6.35 mm, 316 stainless steel tube also located inside the black iron pipe support. Inside the duct the calibration line is brought out through the black iron pipe and connects with a 316 stainless steel tee located between the duct valve and the filter holder. When calibration gas is introduced under pressure, the check valve is closed and the calibration gas passes through the filter (the check valve poppet was removed from both systems in the course of the program, see Discussion section).

The mechanical support for the probe is taken through a pipe cap modified into a port connector and probe clamp. This connector was screwed into the existing port bushing in the duct wall.

CALIBRATION AND SAMPLING LINES

Calibration lines from gas tank regulators to the sample probe assembly were 6.35 mm o.d. x 0.076 mm wall polypropylene. Fittings were nylon compression type.

All indoor sampling lines were 6.35 mm, o.d. x 0.076 mm wall polypropylene tubing. All outdoor sampling lines were electrically traced Teflon tubing Dekoron TM type 2150-045. This tubing was used since it is less expensive than fabricating long sections of heated polypropylene tubing.

Heating was used only to prevent the sample from freezing in the sample line. Power to heat the lines was controlled by a variable transformer. Voltage settings were determined from the DekoronTM technical literature on

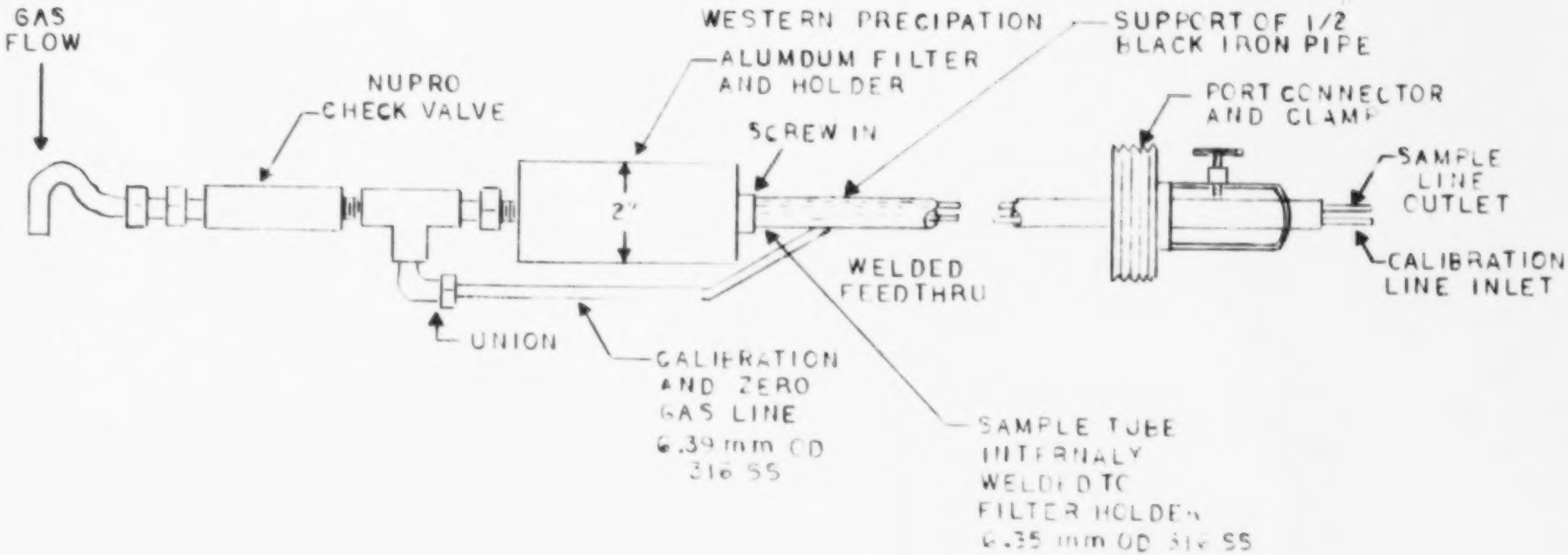

GAS FLOW
NUPRO CHECK VALVE
WESTERN PRECIPATION
ALUMDUM FILTER AND HOLDER
2"
SCREW IN
SUPPORT OF 1/2 BLACK IRON PIPE
PORT CONNECTOR AND CLAMP
SAMPLE LINE OUTLET
CALIBRATION LINE INLET
WELDED FEEDTHRU
UNION
CALIBRATION AND ZERO GAS LINE 6.39 mm OD 316 SS
SAMPLE TUBE INTERNALY WELDED TO FILTER HOLDER 6.35 mm OD 316 SS

Figure II-4. Probe Assembly.

temperature rise above ambient for power input. The voltage settings were calculated to provide about a 5°C temperature rise above minimum expected ambient temperatures. An attempt was made to monitor the temperature of the sample gas exiting from the heated tubing using thermocouples and a recorder. However, recorder difficulties precluded these measurements.

The approximate length of each type of tubing for the two sites are shown in Table II-1.

TABLE II-1.

APPROXIMATE LENGTHS OF SAMPLING LINE
FROM PROBE TO INSTRUMENT RACK

LINE	OIL-FIRED SITE	COAL-FIRED SITE
Dekoron^{TM}	9m	20m
Polypropylene	20m	1.5m

INSTRUMENT RACKS

Other than the probe assembly and sampling lines the monitoring systems were packaged into instrument racks. The locations of the instrument racks at the test sites are shown in Figures II-2 and II-3. These racks included the following:

1. analyzers
2. sample pump
3. moisture removal equipment
4. recorders
5. automatic and manual calibration control
6. calibration gases

The scheme was similar for both the oil-fired and coal-fired sites. However, the choice of analyzer dictated differences in the moisture removal equipment. The oil-fired site was equipped with a NDUV (DuPont Model 400) SO_2 analyzer and a chemiluminescence (Thermoelectron Model 10A) $NO-NO_x$ analyzer. As discussed in Part One these analysis methods required only the removal of liquid water from the sample stream. Figure II-5 shows schematically the sample and calitration gas connections. The tubing lengths are shown. All tubing was 6.35 mm o.d. x 0.076 mm wall polypropylene. Figure II-6 shows pictorially the mechanical arrangement of the instrument rack.

The coal-fired site was equipped with a NDIR (INTERTECH) NO Analyzer and an electrochemical cell (Dynasciences) SO_2 Analyzer. The electrochemical cell analyzer requires only the removal of liquid water from the sample stream, but the NDIR Analyzer also requires that the water vapor in the sample stream by held at a constantly low level. For this reason, the sample stream to the NDIR analyzer was passed through a Hankisons refrigerated condenser upstream of the analyzer. The sample and calibration gas connection for the instrument racks is shown schematically in Figure II-7. Tubing was 6.35 mm o.d. x 0.076 mm wall polypropylene. Figure II-8 shows pictorially the front and control panels of the instrument rack.

Components common to both systems were the following:

1. sample pump - Thomas Industries, 107CA110
2. ball float traps - Armstrong, 11-LD
3. flow meters with metering valve - Dwyer, RMS-3-SSV
4. fine filter - glass wool plug in a ~1 cm x 12 cm long diameter glass tube

The calibration system was either automatically or manually controlled. On automatic control, the monitoring system was zeroed and spanned on SO_2 and NO in each 24-hour period. Each calibration gas was passed through the system for approximately 10 minutes. The circuit diagram for the control system is presented in Part I. The calibrations were prepared and analyzed by Matheson Gas products and supplied in 1A cylinders. The zero gas was nitrogen and the SO_2 and NO preparations were in nitrogen.

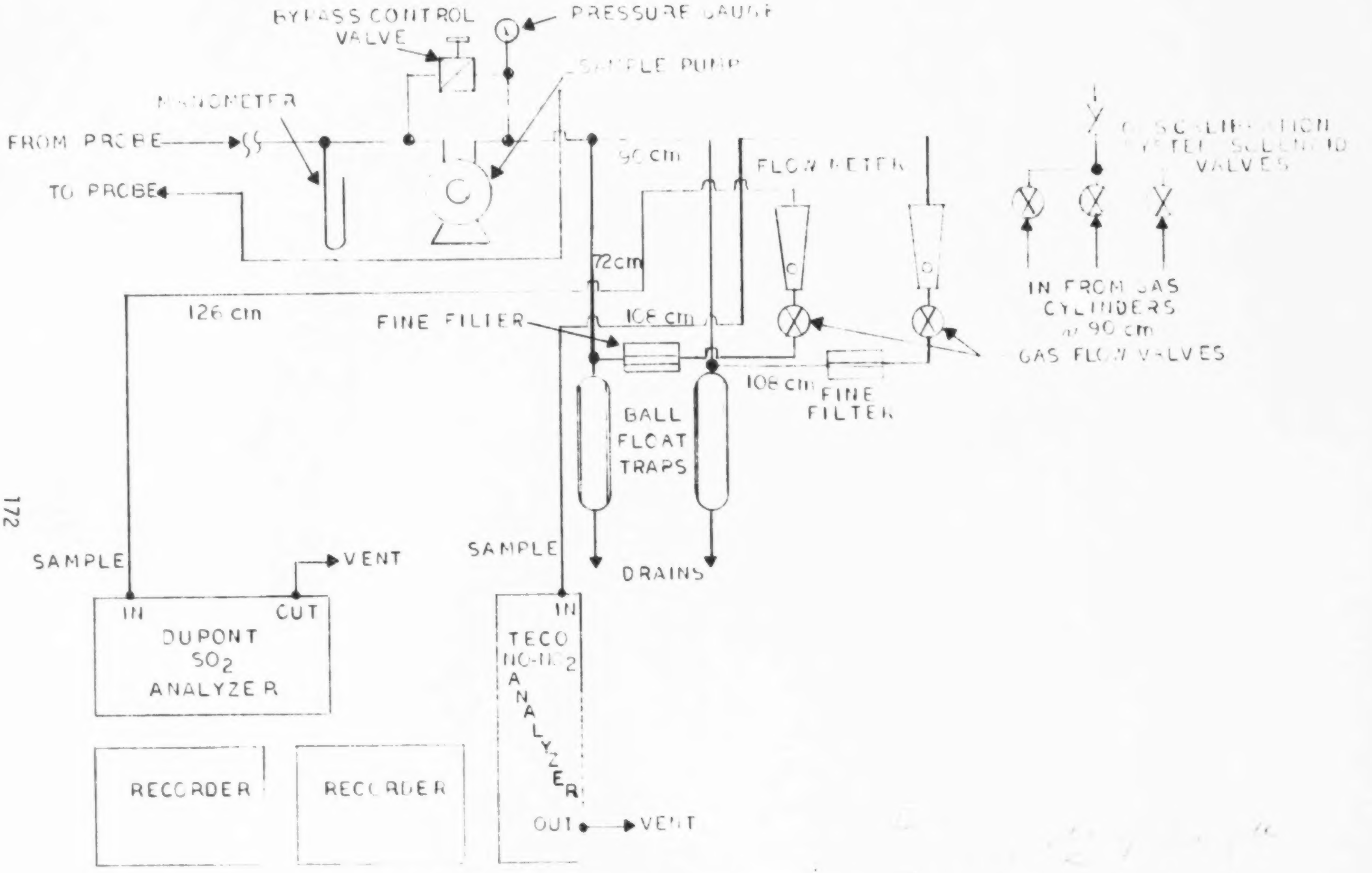

BYPASS CONTROL VALVE
PRESSURE GAUGE
SAMPLE PUMP
MANOMETER
FROM PROBE
TO PROBE
90 cm
72cm
126 cm
FINE FILTER
108 cm
FLOW METER
108 cm
FINE FILTER
GAS CALIBRATION SYSTEM SOLENOID VALVES
IN FROM GAS CYLINDERS @ 90 cm
GAS FLOW VALVES
BALL FLOAT TRAPS
DRAINS
SAMPLE
VENT
IN
OUT
DUPONT SO2 ANALYZER
SAMPLE
IN
TECO NO-NO2 ANALYZER
OUT
VENT
RECORDER
RECORDER

Figure II-5. Schematic of Sample and Calibration Gas Connections for Analyzers.

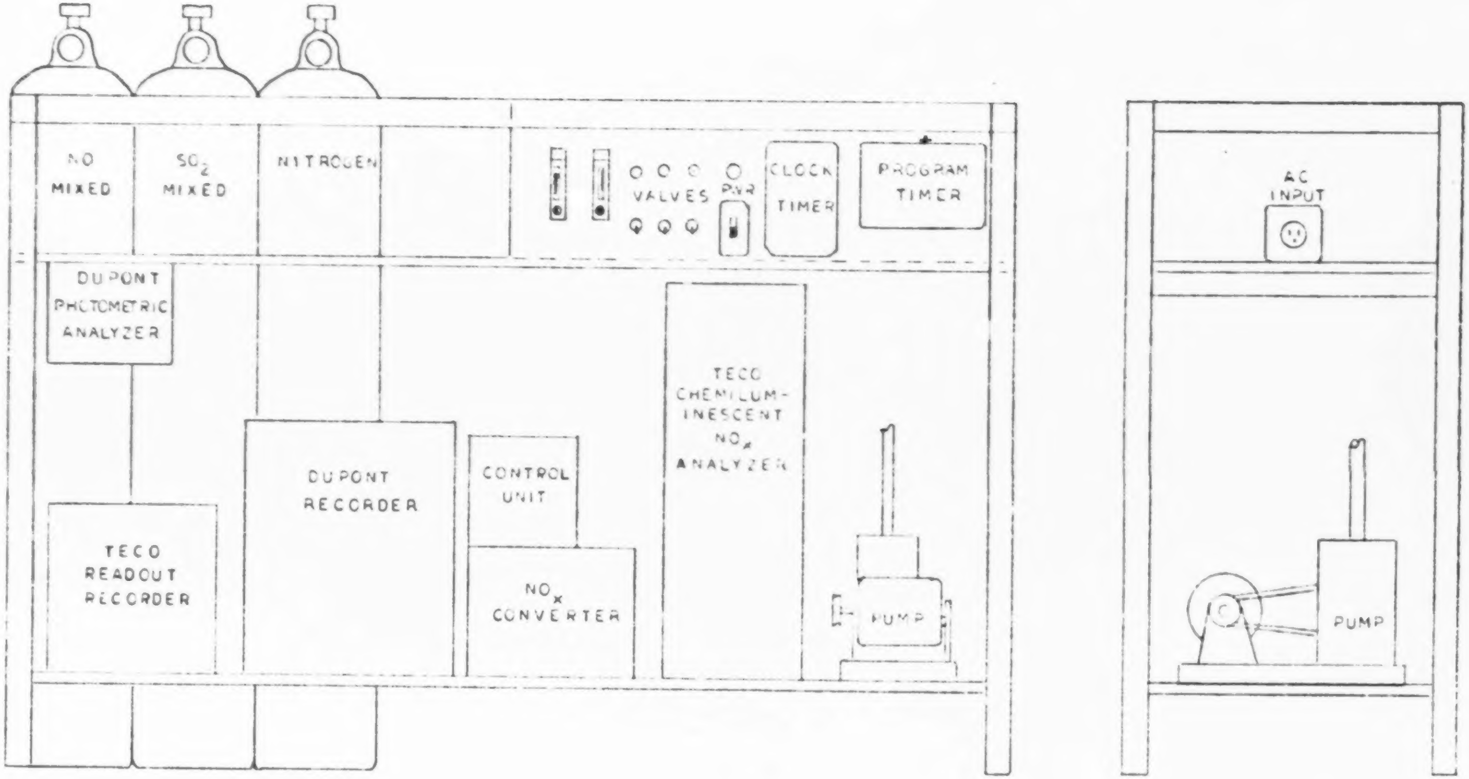

NO MIXED
SO$_2$ MIXED
NITROGEN
VALVES
PWR
CLOCK TIMER
PROGRAM TIMER
DUPONT PHOTOMETRIC ANALYZER
TECO READOUT RECORDER
DUPONT RECORDER
CONTROL UNIT
NO$_x$ CONVERTER
TECO CHEMILUM-INESCENT NO$_x$ ANALYZER
PUMP
AC INPUT
PUMP

Figure II-6. Instrument Rack

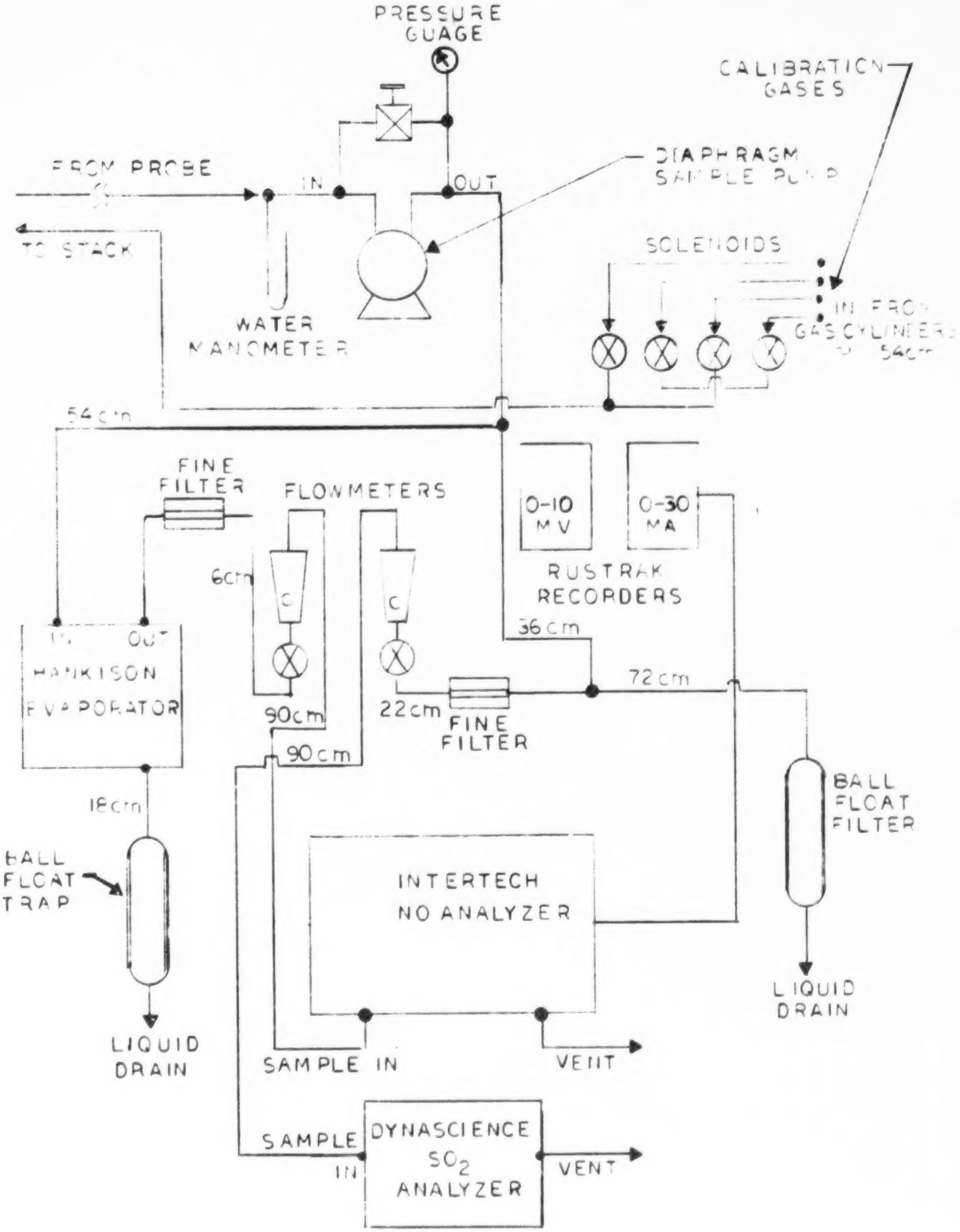

PRESSURE GUAGE
CALIBRATION GASES
FROM PROBE
IN
OUT
DIAPHRAGM SAMPLE PUMP
TO STACK
SOLENOIDS
WATER MANOMETER
IN FROM GAS CYLINDERS
54cm
54cm
FINE FILTER
FLOWMETERS
0-10 MV
0-30 MA
6cm
RUSTRAK RECORDERS
IN
OUT
HANKISON EVAPORATOR
36cm
72cm
90cm
22cm
FINE FILTER
90cm
18cm
BALL FLOAT FILTER
BALL FLOAT TRAP
INTERTECH NO ANALYZER
LIQUID DRAIN
LIQUID DRAIN
SAMPLE IN
VENT
SAMPLE IN
DYNASCIENCE SO_2 ANALYZER
VENT

Figure II-7. Schematic of Sample and Calibration Gas Connections for Instrument Racks.

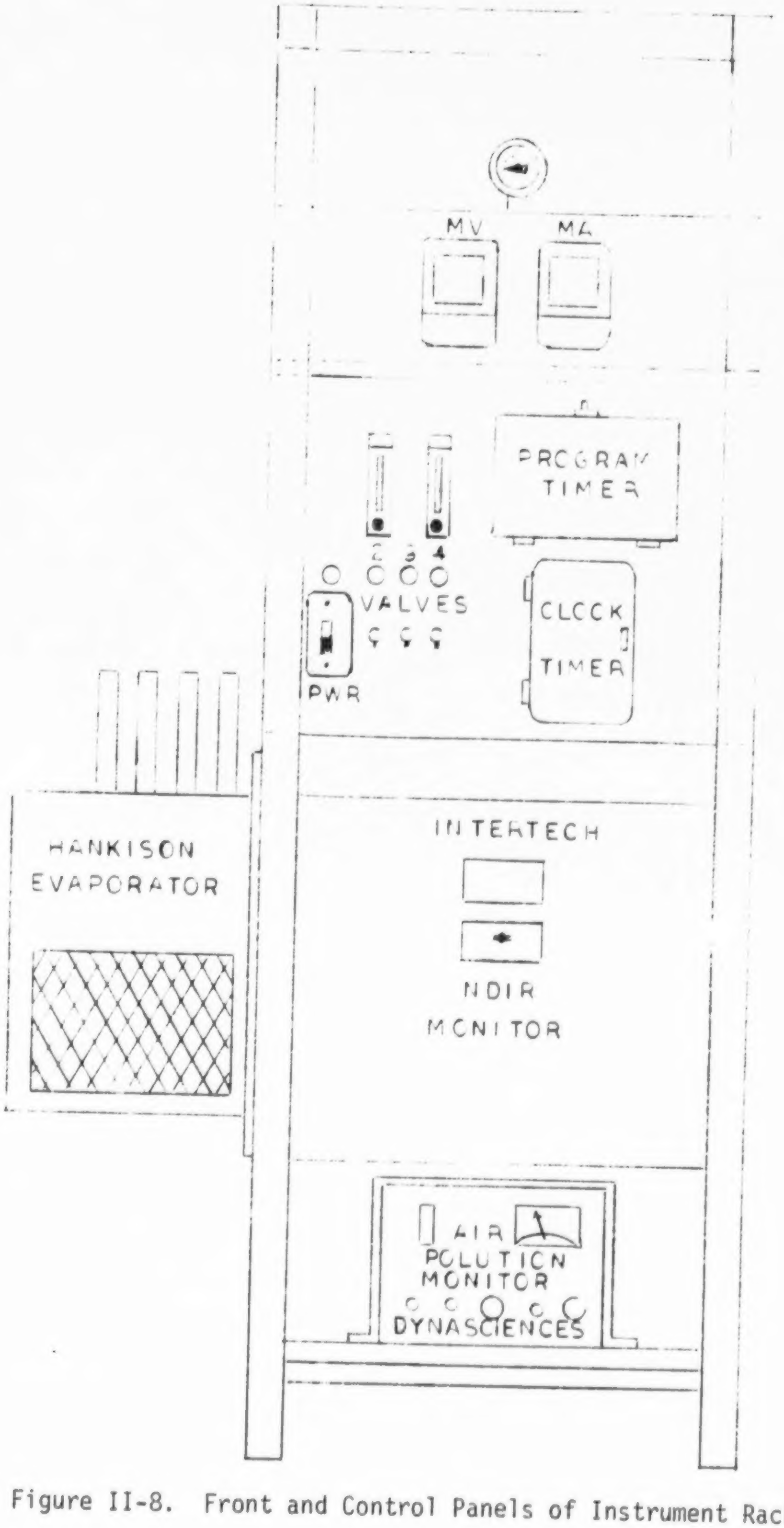

MV
MA
PROGRAM
TIMER
2 3 4
VALVES
PWR
CLOCK
TIMER
HANKISON
EVAPORATOR
INTERTECH
NDIR
MONITOR
AIR
POLUTION
MONITOR
DYNASCIENCES

Figure II-8. Front and Control Panels of Instrument Rack.

OPERATION

GENERAL

In preparation for the field demonstrations, the instrument racks were fabricated in the Walden shops. While fabrication was underway, a particulate survey was made of both sites by EPA Method 5, and the sampling and calibration lines installed between the intended probe and instrument locations.

After fabrication of the racks, operability was tested in the laboratory for sample flow, automatic calibration sequence, recorder operation and moisture removal from sample stream. Then the instrument racks and probes were installed: the first at the oil-fired site, and the second at the coal-fired site.

The problems of start-up, i.e., setting flow rates, setting pressures, setting calibration timers, checking for leaks, setting power for heated sample lines, etc., required more attention and time than was initially anticipated.

OPERATIONAL DATA

Table II-2 is a compilation of the operating data of the monitoring system by test site.

OPERATIONAL PROBLEMS

The following is a discussion of problems that were encountered during the operation of the system.

During the initial operation of the system at the oil-fired site beads of water in the polypropylene tubing were noticed downstream of the traps and the glass wool of the fine filters was soaked. It was suspected that condensate flowing into the pump was being re-evaporated as the sample was heated up in the pump. Indeed to the touch, the sample line into the pump was noticably cooler than the outlet line. Evidently condensation in the sample gas was still occurring after the ball-float trap. To correct this situation

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TABLE II-2

OPERATIONAL DATA

FUNCTION	OIL-FIRED SITE	COAL-FIRED SITE
Sample flow	$\sim$ 2 l/min	$\sim$ 2 l/min
Pump suction	3.0 kN-m^{-2}	3.0 kN-m^{-2}
Pump pressure*	20-40 kN-m^{-3}	20-40 kN-m^{-2}
Heated tubing setting	35 volts	30 volts
SO_2 span gas	381 ppm	1070 ppm
NO span gas	490 ppm	790 ppm
Calibration Gas Pressure**	$\sim$ 40 kN-m^{-2}	$\sim$ 40 kN-m^{-2}
Room temp. at instrument rack	$\sim$ 33°C	$\sim$ 28°C

---

[*] Pulsations in the flow at the exit of the pump made the pressure guage needle fluctuate between the readings.

[**] Pressure was set as low as regulator would permit

a cooling coil of about 1 m of polypropylene material was made and inserted between the pump and the ball-float trap. Then the fine filter which was connected with a short line to the ball-float trap was relocated close to the flow meter (about 1 m of sampling line down-stream) and the sample line pitched so as to drain any condensate in this line back into the trap. The cooling coil alteration worked well enough so that no condensate was noticed forming after the traps.

During most of the demonstration period the boiler at the oil-fired site was shut down. These shut downs were a result of a fuel saving scheme throughout the Northeast during the energy crisis of the winter of 1973-1974. While the coal-fired site also had shutdowns during this period, these were not as frequent or for as long a duration as the oil-fired unit. (See Table II-3). The shutdowns of the coal-fired plant were the results of equipment breakdowns. These shutdowns made the continuous operation of the equipment difficult (coal-fired) to impossible (oil-fired).

At the oil-fired plant, it was found that the check valve at the probe tip seemed to work well until the boiler was shut down and then restarted. After this cycle the check valve was found stuck in the closed position after calibration. The probe was removed and the valve examined visually. There was an apparent caking of particulate matter around the poppet of the check valve. It was reinstalled and it operated correctly until the next boiler shutdown-startup cycle then the problem re-occured. At this time, the check valve was removed from the system and calibration was performed by gas flooding (injecting more calibration gas at the probe tip than was sampled). Later at the coal-fired site the check valve was observed to stick open. This was at the conclusion of the demonstration. Hence, the expense of gas flooding is preferred over the low reliability of the check valve approach, at least for the particular valve chosen.

TABLE II-3

PLANT OPERATION

1973	PLANTS		1974	PLANTS	
DATE	OIL	COAL	DATE	OIL	COAL
12/12	On	On	1/1	Off	On
12/13	Off	On	1/2	Off	On
12/14	Off	On	1/3	Off	On
12/15	Off	Off	1/4	Off	On
12/16	Off	Off	1/5	Off	On
12/17	Off	Off	1/6	Off	Off
12/18	Off	On	1/7	Off	Off
12/19	Off	On	1/8	Off	Off
12/20	On	On	1/9	Off	Off
12/21	On	On	1/10	Off	Off
12/22	On	On	1/11	*	Off
12/23	On	On	1/12		Off
12/24	On	On	1/13		Off
12/25	On	On	1/14		Off
12/26	On	On	1/15		Off
12/27	Off	On	1/16		On
12/28	Off	On	1/17		On
12/29	On	On	1/18		On
12/30	Off	On	1/19		On
12/31	On	On	1/20		On
			1/21		On
			1/22		*

* Instruments removed from test site

Shortly after beginning the demonstration program the chemiluminescent analyzer failed due to an insulation breakdown in the high voltage power supply for the ozone generator. This failure was not a result of the sampling interface system.

During a time when the oil-fired site was not attended the manometer fluid upstream of the pump was sucked into the system. It is believed that this problem was caused by the check valve sticking closed. As a precautionary rough measure the manometers were removed from both systems.

Almost from the onset there was difficulty maintaining constant flow through the system at the coal-fired site. The flow rate tended to decrease steadily. Originally it was thought that the pump bypass control valve setting was changing due to vibration. The valve was replaced, but the problem persisted. Then the pump was removed and the head disassembled. Inspection showed that the read valves were not operating properly because of the collection of a dark, ash-appearing crust with a slight greenish tinge. This pump had about 500 hours of sampling operation. The replacement pump failed completely by the end of the program with less operation time.

At the coal-fired site condensate flooded the system due to inadequate gas-liquid separation at both the ambient temperature trap and at the refrigerated trap. Inspection of the refrigerated trap following the condensor revealed inadequate designing. The sample flow was over the trap inlet but not through the ball-float trap itself. Visual inspection showed no reason why the subsequent ambient level trap failed to separate, and in a test of pouring water into the sample intube, the trap functioned properly. The program ended as system modifications were being implemented to remedy this problem.

The weather caused operational and safety problems principally by limiting the field crew activities. During the course of the field program, ambient temperatures were frequently below freezing with snow and freezing rain common. These conditions interferred to a major degree with the manual sampling of the flue gas, and somewhat with the operation of the equipment. A weather related problem which had not been accounted for in the sampling interface design, is when a boiler shuts down with a below freezing temperature. At the coal-fired site there was such a shutdown and condensate in the probe external to the stack froze and blocked the sample, requiring probe removal for thawing. During operation this point of the probe was maintained above freezing by the hot sample gas flow. Installation of electric heaters on the probe which could be turned on during a re-start of the system after shut down will correct this difficulty.

DATA

Instrumental and manual data were taken on both the oil-fired and coal-fired flue gases. Due to the difficulties described in the previous section, the volume of data collected is limited. Background data on particulate loadings (EPA Method 5) and gas composition were taken before installing the sampling systems. These data are shown in Table II-4. From the monitoring systems, data were taken on response times. These data are shown in Table II-5. Simultaneous manual and instrumental measurements were made on the flue gases. The manual measurements were EPA Method 6 for SO_2 and EPA Method 7 for NO_x.

The manual and instrumental data are shown in Tables II-6, II-7, and II-8.

The agreement of the instrumental methods with the manual methods is fairly good, confidence in the values for the NDIR instrument is poor. The range of the manual NO_x data seems large for this type of process stream. However the reproducibility of Method 7 results has been reported as 7% of value for a one standard deviation interval*. This explains in part variations in the manual data. The small mean difference for the widely scattered results in Table II-8 is explicable as chance.

Two of the Method 6 results in Table II-7 were excluded from the analysis because the very low Method 6 results occurred for samples for which ice was observed in the peroxide collection solutions in the impinger train.

The zero and span data are variable. It is suspected that flow changes, due to the pump problem discussed before, affected the response. These problems precluded the use of these data to establish instrumental performance changes due to operation life. In fact, the strip chart data is in a state which precluded data reduction.

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* Hamil, H. F. and D. E. Camann, "Collaborative Study of Methods for the Determination of Nitrogen Oxide Emission from Stationary Sources (Fossil Fuel Fired Stream Generator): EPA Contract No. 68-02-0623, Southwest Research Institute, San Antonio, Texas (December 10, 1973).

TABLE II-4

BACKGROUND DATA

	COAL-FIRED			OIL-FIRED			
TEST	1	2	3	1	2	3	(UNITS)
Mass loading	95.9	203	161	99.3	62.4	81.7	$mg\text{-}m^{-3}$
Average		153			81.2		$mg\text{-}m^{-3}$
Gas Moisture	7.24	6.32	5.17	10.66	10.03	11.94	%
CO_2	14	14	14	8	8	8	%
O_2	5	5	5	9.5	9.5	9.5	%
N_2	81	81	81	82.5	82.5	82.5	%
Gas Velocity	11.1	11.1	11.1	9.14	9.13	9.17	$m\text{-}S^{-1}$
Date	11/30	12/3	12/[illegible]	11/24	11/24	11/24	

TABLE II-5

RESPONSE TIME TO SPAN GAS FOR INTERFACE SYSTEM PLUS ANALYZERS

	OIL-FIRED	COAL-FIRED
SO_2	1 min.	3/4 min.
NO_x	1/2 min.	2 min.

TABLE II-6

OIL-FIRED PLANT SO_2 DATA

DATE	INSTRUMENTAL NDUV ANALYZER (ppm)	MANUAL EPA METHOD 6 (ppm)	DIFFERENCE INST. - MANUAL (ppm)
12/20/73	210	239	- 30
12/20/73	180	311	- 130
12/20/73	240	297	- 60
12/20/73	250	340	- 90
12/20/73	230	323	- 90
12/20/73	270	327	- 60

Span = 1000 ppm

Mean = $-80 \approx -8\%$ of span

$\sigma = 30$

$$100 \times \frac{3.92\sigma}{\text{span}} = 12\% \text{ (95\% confidence interval)}$$

TABLE II-7

COAL-FIRED PLANT SO_2 DATA

DATE	INSTRUMENTAL ELECTROCHEMICAL CELL ANALYZER (ppm)	MANUAL EPA METHOD 6 (ppm)	DIFFERENCE INST. - MANUAL (ppm)
12/18/73	1300	1470	- 200
12/18/73	1300	164	**
12/18/73	1200	227	**
12/18/73	*	227	-
12/18/73	*	2025	-
12/18/73	*	1476	-
12/18/73	1400	1443	0
12/26/73	1500	1605	- 100
12/26/73	1400	1788	- 400
12/26/73	1400	1777	- 400
12/26/73	1400	1734	- 300
12/26/73	*	1680	-
12/26/73	1500	1886	- 400
12/26/73	1000	1734	- 700

Span = 5000 ppm

Mean = -300 ≈ -6% of span

$\sigma = 200$

$$100 \times \frac{3.92\sigma}{\text{span}} = 16\% \text{ (95\% confidence interval)}$$

* Manual Calibrate Interference

** Manual Data Excluded

TABLE II-8

COAL-FIRED PLANT NO_x DATA

DATE	INSTRUMENTAL NDIR ANALYZER (ppm)	MANUAL EPA METHOD 7 (ppm)	DIFFERENCE INST. - MANUAL (ppm)
12/18/73	1100	455	650
12/18/73	1000	1124	- 120
12/18/73	900	1092	- 190
12/18/73	1080	1156	- 80
12/18/73	1000	1295	- 290
12/18/73	900	1177	- 280
12/18/73	960	962	0
12/26/73	1000	757	240
12/26/73	*	624	-
12/26/73	870	792	80
12/26/73	1000	1498	- 500
12/26/73	920	1063	- 100
12/26/73	920	1017	- 100
12/26/73	870	1102	- 230
12/26/73	*	831	-

Span = 1600 ppm

Mean = -70 ≎ -4% of span

$\sigma = 280$

$$\frac{100\text{x}3.92\sigma}{\text{span}} = 54\% \text{ (95\% confidence interval)}$$

The system response times which were taken manually are consistent with the value predicted by the design data in Part One, viz., 3-1/4 minutes. The example used a flow rate of one liter per minute whereas the demonstration system operated at about two liters per minute. The demonstration system also had somewhat shorter sampling and connection lines and smaller back mixing volumes. These differences resulted in faster response times. For the case of the electrochemical cell instrument, the analyzer and not the interface system was the response time limiting element of the monitoring system.

There were some semi-quantitative data collected on the particulate loading on the coarse filters. The alundum thimbles from the oil-fired and coal-fired plants collected 0.33 grams and 0.48 grams of particulate respectively. Laboratory tests indicated that the filter should work with coal fly ash collection as high as about 70 grams in the thimble. Due to down times for both the demonstration system and the boiler, it is not possible to specify with accuracy the cumulative flow through these filters, hence filter life. However, assuming that the systems operated for a total of fifteen days, which is a reasonable estimate, then an operation time of one year on the coal-fired plant without removing the filter for cleaning is to be expected.

DISCUSSION

From the results of this field program many of the elements of a minimum type sampling system were identified by the design data, in particular the following:

A. a simple probe filter without back-flushing

B. low cost polypropylene sample lines (for temperatures above freezing)

C. moisture removal from the sample stream to ambient level dew points for the analysis methods other than NDIR*

Additionally the system can be calibrated by introduction of span and zero gases into the probe tip filter. Gas flooding of the probe upstream of filter with the calibration gases was found to be perferred over the originially designed system (check-valve) on the basis of reliability.

Failure of the sampling systems was associated with inadequate moisture, mist, and fine particulate removal; and sample pump failures. Both demonstration systems were flooded with liquid, the coal-fired plant systems twice. Three sample pumps were available to this program and all three failed. All pumps failed while installed on the coal-fired system; although one pump, which was removed from the oil-fired demonstration system, failed within four hours after installation on the coal-fired system probably from exposure effects from the oil-fired plant sample gases. Since the demonstration system had the moisture removal system after the pump, it is concluded that the sample pump requires the protection of the moisture removal system and probably the protection of a fine particle filter. This arrangement requires a somewhat more complicated approach as indicated in the discussion in Part I. An alternative approach may be to continue to use a post pump moisture removal system with a more expensive sample handling pump; e.g., the type the Metal Bellows Company is developing for handling raw flue gas. These pumps are under development and the field data are not yet available .

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* This was not field demonstrated for the chemiluminescent analyzer due to instrument failure not related to the interface system.

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Considering the system failure in this field program, one is tempted to use a ne plus ultra moisture removal system ahead of the most robust sampling pump available. This approach would not be representative of a "minimum" type system. A "minimum" type system would be some compromise between this over designed approach and the system which was implemented in this demonstration program. The determination of the lowest-cost suitable approach must be established through further field tests. This program has not resolved this issue. Hence, it can only offer the experience of this demonstration as a caveat to the would-be designer that the reliability of any interface system depends upon protection of the sampling pump and protection of the sampling system from flooding.

The approach of this program made a principal departure from the approach of many other practicioners in the requirements for removing condensate from the sample stream. Many designers have indicated that efforts have to be made to reduce the absorption of the sample gases, i.e., SO_2 and NO_x from the sample stream. These efforts included sample lines heated above the sample dew point and condensers designed to remove condensate with a minimum of exposure time to the sample stream. For the reasons described in Part I, this demonstration program used a system which took no precautions against sample absorption in the condensate as the sample and connection lines were operated below the sample dew point. The results indicate that this approach is sufficient. Interface systems for coal- and oil-fired effluents need not go to the expense of trying to reduce absorption losses from the sample stream.

The demonstration of the non-backflushing probe was successful. As indicated in the previous section the filters used in this demonstration could be expected to operate for a year or longer without maintenance. This inline filter design easily permits a through the probe-tip-filter calibration design.

The check-valve arrangement was not successful on the through probe tip filter calibration system. Not unexpectedly, the check-valve proved to be a high maintenance item. However, the gas flooding approach works well. The costs of the higher calibration gas consumption for gas flooding is deemed worthwhile for the reliability gained.

In conclusion this demonstration program vouched for many of the "minimum" type interface system components identified in Part I. However, the reliabilities of the "minimum" type sample pump and condensate removal system were poor. It is not clear at this time just what improvement of these components is required in order to achieve a sufficient system without over design. However, improvements of this nature do not lend themselves to engineering design calculations; rather, they are evolved as a result of trial and error from field experience. Therefore, further field work is required before the complete "minimum" type system can be specified.